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EDITORIAL

This number of the Journal contains articles on investigations carried out by the Chemical Division of the Institute, some of them in collaboration with the staff of the London Advisory Committee for Rubber Research (Ceylon and Malaya).

It will be observed that a number of these investigations have given negative results, that is, the methods of treatment investigated have not produced any modification in the raw rubber to render it especially adaptable for the purpose in view.

In all scientific work, however, negative as well as positive results have a value and the publication of such results is advisable for record purposes and for the information of other workers on similar problems. Hence the publication of the results of several investigations of this nature in this number of the Journal.

THE SPECIFIC GRAVITY OF LATEX

The value of accurate data in respect of the relationship between the specific gravity of latex and its dry rubber content has considerable importance, especially owing to the increasing applications of latex for the manufacture of various articles.

The determination of the relationship between the specific gravity and dry rubber content in the case of normally preserved (ammoniated) estate latex as well as that of fresh latex, before the addition of ammonia for preservation, is also of importance. Previous information in respect of preserved latex is scanty and the published results have been obtained on a comparatively few samples. The figures now presented are derived from a large number of samples of latex obtained from nine different estates. They include also figures for concentrated latex prepared by centrifugal treatment from which a large proportion of the serum

has been removed and also figures for ordinary latex from which some of the "heavy solids" have been separated by sedimentation after preservation and storage.

Dr. Rhodes has also, by mathematical analysis of the data obtained, indicated the probable value of the specific gravity of the rubber or disperse phase in normal preserved latex and the figure thus obtained is shown to be in close agreement with that estimated by Scholtz and Klotz from determinations on a much smaller number of samples of fresh latex.

The specific gravity of the true rubber phase (caoutchouc) is probably even below the figure now given.

Properties of Clone Rubber

In an article entitled "The Properties of Clone Rubber" Dr. Wiltshire describes the results of investigations on rubber from certain Malayan clones on which previous investigations and data were published in respect of daily variations in the vulcanisation properties of these clones over a period of six months.

In the present investigations are recorded observations on monthly average samples over a further period of two years. The results show that in the four clones studied over this period there are small but characteristic differences in rate of cure and that two of the clones give a faster-curing rubber than the other two. It is possible that other clones may even show greater significant differences in respect of the vulcanising properties of their rubber.

The variations in any one month in the rubber from the different clones is also less than the variation within any one clone over the period. The rate of cure appears to follow approximately the rainfall but there is a period of low values after the wintering season which is not correlated with rainfall.

The seedling rubber shows similar variations in respect of rate of cure.

The importance of the continuation of investigations of this problem, in relation not only to rate of cure, and to other properties of raw rubber derived from clones, but also its extension to other well-known clones already planted on a commercial scale is realised. Unfortunately the clones examined in this investigation provide the only material yet available in Malaya for such work. Considerable additional material will however be available in the near future.

Sulphuric Acid as a Coagulant

As many planters are aware, a prejudice exists among many rubber manufacturers in respect of the use of raw rubber from latex coagulated with sulphuric acid.

The use of this acid was condemned by the Rubber Growers' Association and by the writer as a result of investigations some years ago. It was however realised, even at that time, that the use of minimum quantities of the acid was not likely to have any harmful effect, but that it could only be used within much narrower limits than acetic or formic acids, without causing considerable variability in the vulcanising properties of the rubber.

On account of the satisfactory market price of raw rubber, until recently, there has also been no dire necessity nor incentive for the producer to substitute sulphuric acid for acetic or formic acid as a coagulant, although we are aware that a few estates have used the acid—not on the advice of this Institute nor of former rubber research organizations of Malaya—for many years without receiving any complaints from their buyers or from any consumers.

Apparently it has been assumed that this Institute is definitely recommending the use of sulphuric acid as a coagulant. If readers however will refer again to the article by Dr. Wiltshire published in the Journal (Vol. 4 (1932) p.94) they will appreciate that the position was very clearly stated and that both the advantages and disadvantages of using this acid were discussed. It may also be emphasized that the further investigations were made and the article published as a result of enquiries received from various producers.

The present Journal contains a report by Messrs. Martin & Davey of the London Advisory Committee for Rubber Research (Ceylon and Malaya) laboratories, on the examination of samples sent from this Institute, and includes observations made by the India Rubber Manufacturers' Association, Great Britain. Drs. Rhodes and Wiltshire have also appended a "Discussion and Recommendations" on the problem.

The report now published and the discussion and recommendations present a clear picture of the position, which it is hoped will be of value to both manufacturers and producers.

At present, it can be stated that sulphuric acid is being used as a coagulant on only a few Malayan rubber estates.

Rubber from dilute Latex

The report of investigations on samples of sheet and crepe rubber from excessively diluted latex by Messrs. Martin, Davey,

Baker and Rhodes is a part of a more complete investigation which is being undertaken in collaboration with the London Advisory Committee for Rubber Research (Ceylon and Malaya) and with the Technical Research and Development of New Uses Committee of the Rubber Growers' Association on three problems viz., (a) the preparation of a raw rubber which on vulcanization will produce odourless manufactured articles, (b) the preparation of a more plastic raw rubber and (c) the preparation of a raw rubber having low moisture-absorption properties for use in the electrical industries. The results of the investigation indicate that rubber from the dilute latex is not more plastic than that from normal latex as diluted on the estate for the preparation of ordinary sheet and crepe, although it would become softer on storage.

The water-absorption capacity of rubber from dilute latex is low but does not differ sufficiently from that of normal sheet and crepe to warrant the preparation of raw rubber from very dilute latex.

Rubber from Autoclaved Latex

The investigations reported under this heading refer to a method of heating latex under pressure in order to ascertain the effect on the resultant rubber with particular reference to its plasticity. The treatment is therefore a method for modifying the actual rubber (caoutchouc) in contrast to the addition of softeners to the latex or the raw rubber for a similar purpose.

The results of the investigations however indicate that the method of treatment, which involves special plant and extra cost of preparation, is unlikely to be of value for the purpose in view.

The Effect of "Plastogen" and Bitumen on Rubber

In an attempt to produce a softer or more plastic rubber desired by manufacturers, experiments have been carried out with the addition of a proprietary softener "Plastogen" direct to latex. This softener is stated to be in use by manufacturers for addition to dry raw rubber. It was also thought that it might be useful to ascertain the effect of bitumen emulsions with latex for a similar purpose, since bitumen is also used by manufacturers for incorporation with rubber mixtures as a softener.

The results of these investigations are described in two articles entitled "Note on the Incorporation of a Rubber Softener with Latex and its Effect on the Plasticity of Rubber" and "Rubber from Latex-Bitumen Mixtures".

The investigation of the softener "Plastogen" when added to latex indicates that rubber produced in this manner has

little or no commercial prospects, since the product is not sufficiently soft to warrant acceptance as a rubber for which a premium might be obtained.

The results of the investigations on the latex-bitumen emulsion product also show that rubber prepared in this manner would not have any commercial prospects.

It is very unlikely that any such mixtures with raw rubber prepared on estates would find a market. Some other method of producing a more plastic product, by which the rubber itself is modified, must be sought.

Paranitrophenol in the Preparation of Crepe Rubber

A few years ago paranitrophenol was recommended by the Scientific Officers of the Rubber Growers' Association Laboratories, Malaya, as a fungicide for the prevention of the development of moulds in raw rubber. It was used extensively in the preparation of sheet rubber, especially during the previous period of control of rubber export from Malaya when considerable quantities of raw rubber were stored on some estates.

As far as the writer is aware however it has never been used in Malaya for the treatment of thin pale crepe, since it produces a yellowish colour in the product treated.

We have been asked however by the London Advisory Committee for Rubber Research (Ceylon and Malaya) to draw attention to the undesirability of using this chemical in the preparation of crepe rubber. The note entitled "Objections to the Use of Paranitrophenol in the Preparation of Crepe Rubber" has been written with this object.

THE SPECIFIC GRAVITY OF PRESERVED LATEX

BY

EDGAR RHODES

Introduction

The literature on latex contains a number of references to the specific gravity of fresh latex but published information on the specific gravity of preserved latex in the condition in which it reaches the consumer appears to be practically non-existent. De Vries (1 & 2) and Scholtz and Klotz (3) investigated the specific gravity of undiluted fresh latices of various dry rubber contents and, from their results, each deduced the specific gravity of the disperse or rubber phase. The average specific gravity of the rubber globule as deduced by De Vries is 0.914. Scholtz and Klotz's value for the disperse phase is 0.901 which is appreciably lower than that of De Vries.

Although the published literature contains no references to the specific gravity of commercial preserved latex, the Rubber Trade Association of London gives a table of values in its latex contract forms, but details are lacking as to the total number of experimental observations which the table represents. A significant feature is that, by extrapolation of the dry rubber content values to 100 per cent., after the manner of Scholtz and Klotz, the figures obtained for the specific gravity of the rubber disperse phase is 0.912, which agrees fairly well with that of De Vries for fresh latex and which is considerably higher than that of Scholtz and Klotz.

In view of the paucity of information available on the specific gravity of preserved latex it seemed desirable to obtain additional data and incidentally to make a further check on the published values for the specific gravity of the rubber disperse phase.

The primary object was to construct, after the manner of the Rubber Trade Association, a specific gravity table which might reasonably be said to be representative of average commercial preserved latex over a fairly wide range of dry rubber contents. De Vries and Scholtz and Klotz have both shown that, with fresh latices of any given dry rubber content, appreciable variation in specific gravity is found. Seasonal variations in the amount of serum constituents and similar variations due to the nature and severity of the tapping system employed, together with accidental or deliberate dilution of latex with water in the

field, combine to produce specific gravity variations in latices of the same dry rubber content. In working with preserved latex there is an additional variable, in the amount of ammonia present and in the form in which the ammonia is added. In attempting to prepare a table for average commercial preserved latices it is obviously important therefore to examine a large number of samples from a reasonable number of different sources.

The findings of Scholtz and Klotz are based upon an examination of 85 samples, all of which were taken from the same estate source and a number of them from individual trees on the experimental area. In the present work individual tree samples have been rigidly excluded, the latex has been drawn from a number of different estates and the total number of samples examined is ten times that of Scholtz and Klotz.

Section A

Experimental

Sources of Latex

In Table I below the various sources of latex are set out while column 3 of Table II indicates the sources of the samples in various zones of dry rubber content.

TABLE I

Sources of Latex

Estate No.	District	Latex from
1	Negri Sembilan	Seedling trees
2	Selangor	" "
3	"	" "
4	"	Seedling trees and four clones
5	"	Seedling trees
6	Johore	" "
7	Selangor	" "
8	"	" "
9	"	" "

The samples were collected as opportunity offered over a period of approximately six months, and the attempt was made to cover the approximate normal range of dry rubber contents, 28—50 per cent. It is unlikely that commercial preserved latex will ever be required at a dry rubber content less than 28 per cent. while the tree itself fixes the dry rubber content of 48—50 per cent. as the richest latex which can be shipped in any quantity without artificial concentration. The majority of the samples having dry rubber contents in the range 28—32 per cent. were obtained from an area on Estate No. 2 which is being tapped on a fairly drastic system as a preliminary to re-planting. On this estate the chances of deliberate dilution of latex by the tappers in the field were small and samples were not drawn for test on wet days. Latex of high dry rubber content, in the zone 46—50 per cent. is difficult to obtain in quantity, and a large proportion of the samples in this zone were of necessity obtained from Estates Nos. 2 and 7 which happen to be two of the few Malayan estates which export unconcentrated latex of high dry rubber content.

Sampling and Preservation

It was not possible, except in a few cases, to draw samples from daily bulks of latex from a whole estate or estate division, chiefly because the time required for the accumulation of a sufficiently large number of separate test samples would have been far too long. In order to make possible the collection of a suitable number of samples in a reasonable time, the yield from a tapper's task of 250—300 trees was taken as a suitable bulk from which a sample might be drawn. By this means it was possible to collect from any estate on a given day a number of samples, each of which represented the mixed product from a fair tree population. The adoption of this procedure introduced, in nearly all cases, the necessity of preservation with liquid rather than with gaseous ammonia. The addition of liquid ammonia as a preservative has the two-fold effect upon the specific gravity of slight aqueous dilution, together with a reduction due to the ammonia itself. The dilution effect is however by no means so great as the accidental or deliberate dilution which is very common in commercial practice, as for instance when rich latex of 42—43 per cent. dry rubber content is deliberately diluted with water at the factory to 38—39 per cent. before shipment, and the use of liquid ammonia in the preservation of the test samples is not therefore unwarranted. The permissible range of ammonia content was taken as 0.5—0.7 per cent. and any sample containing an amount of ammonia within this range was accepted for test.

Dry Rubber Content and Specific Gravity Determination

Dry rubber contents were determined in duplicate on each sample after thorough shaking, by the method described by Bishop and Fullerton (4). Values for dry rubber content were thus obtained as weight percentages or in other words as the weight of dry rubber contained in a given weight of latex.

Specific gravity determinations were also made in duplicate on each sample by the specific gravity bottle method, after very thoroughly shaking each sample to re-disperse settled solids. No temperature refinements were introduced. These were scarcely warranted by the very nature of the investigation and its uncontrollable variations. In any case, room temperature at the Institute is always very constant in the region 29°—30°C.

Results

In all, 852 samples were examined for dry rubber content and specific gravity; the dry rubber content range covered was 28—50 per cent. approximately. The results were then tabulated according to dry rubber content into groups of two units after the manner of the Rubber Trade Association in the presentation of its values. In this way, the total dry rubber content range was divided arbitrarily into eleven groups. The number of individual samples falling into each group naturally varied, the most populous group containing 117 individuals and the least populous 38 only. This unequal distribution was unavoidable. For each group of two dry rubber content units, the mean dry rubber content and the mean specific gravity was then calculated. Columns 1, 2, 4 and 5 of Table II present the values so obtained.

Analysis of Results

It was expected that the eleven values for mean specific gravity at the corresponding mean dry rubber content values, set out in columns 4 and 5 of Table II, would not lie exactly in a straight line and a mathematical analysis of the spread of the individual specific gravity values in each group, about the mean for that group, was made in order to determine the significance of each of the means. The standard deviation of the individual values from the mean was calculated for each group, together with the corresponding probable error. Similarly, the standard deviation and probable error of the mean itself were obtained; these are set out in columns 6, 7, 8 and 9 of Table II. In examining the values for the standard deviation and probable error of a single determination, it is seen that, even in the two worst groups, the chances are even that a single determination falls

TABLE II

Specific Gravity and Dry Rubber Content for 852 samples of preserved latex

Group D.R.C. per cent. by weight	Total Samples in Group	Sources (see Table I)	Mean D.R.C.	Mean Specific Gravity	Specific Gravity Distribution					
					About the arithmetic Mean		Standard Deviation of Arith. Mean	Probable Error of Arith. Mean	About the Line $s = -0.001158\ t + 1.0177$	
					Standard Deviation	Probable Error			Standard Deviation	Probable Error
			(t)	(s)	ó	0.6745 x ó	óm	0.6745 x óm	ó	0.6745 x ó
1	2	3	4	5	6	7	8	9	10	11
28.1 — 30.0	97	1,2,3,	29.3	0.9831	±0.0012	±0.0008	±0.00012	±0.00008	±0.0014	±0.0009
30.1 — 32.0	116	1,2,4	31.0	0.9820	±0.0012	±0.0008	±0.00011	±0.00008	±0.0011	±0.0008
32.1 — 34.0	47	1,2,3, 4,5	33.0	0.9796	±0.0019	±0.0013	±0.00028	±0.00019	±0.0017	±0.0012
34.1 — 36.0	59	1,2,3,4,5	35.2	0.9773	±0.0022	±0.0015	±0.00029	±0.00019	±0.0021	±0.0014
36.1 — 38.0	117	1,2,3 4,5,6,7,8,9	37.3	0.9744	±0.0022	±0.0015	±0.00020	±0.00013	±0.0020	±0.0013
38.1 — 40.0	102	1,2,3,4, 6,7,8,9	39.1	0.9725	±0.0015	±0.0010	±0.00015	±0.00010	±0.0014	±0.0009
40.1 — 42.0	104	2,4,6,7	40.9	0.9705	±0.0014	±0.0009	±0.00014	±0.00010	±0.0015	±0.0010
42.1 — 44.0	39	2,4,5,6,7	43.0	0.9682	±0.0020	±0.0014	±0.00032	±0.00022	±0.0018	±0.0012
44.1 — 46.0	38	2,4,5,7	45.2	0.9650	±0.0017	±0.0011	±0.00028	±0.00019	±0.0014	±0.0009
46.1 — 48.0	85	2,4,7	47.1	0.9626	±0.0012	±0.0008	±0.00013	±0.00009	±0.0012	±0.0008
48.1 — 50.0	48	2,6,7	48.8	0.9614	±0.0009	±0.0006	±0.00013	±0.00009	±0.0010	±0.0006
	852								±0.0015	±0.0010

within ±0.0015 of the corresponding mean specific gravities for these groups. The standard deviation of the means themselves about the true mean, which would result from an infinite number of determinations, is in the worst case ±0.00032, while in six of the eleven groups it is ±0.00015 or less. Even in the worst case the chances are even that the arithmetic mean lies within ±0.00022 of the true value, while in seven of the eleven groups the probable error does not exceed ±0.00013.

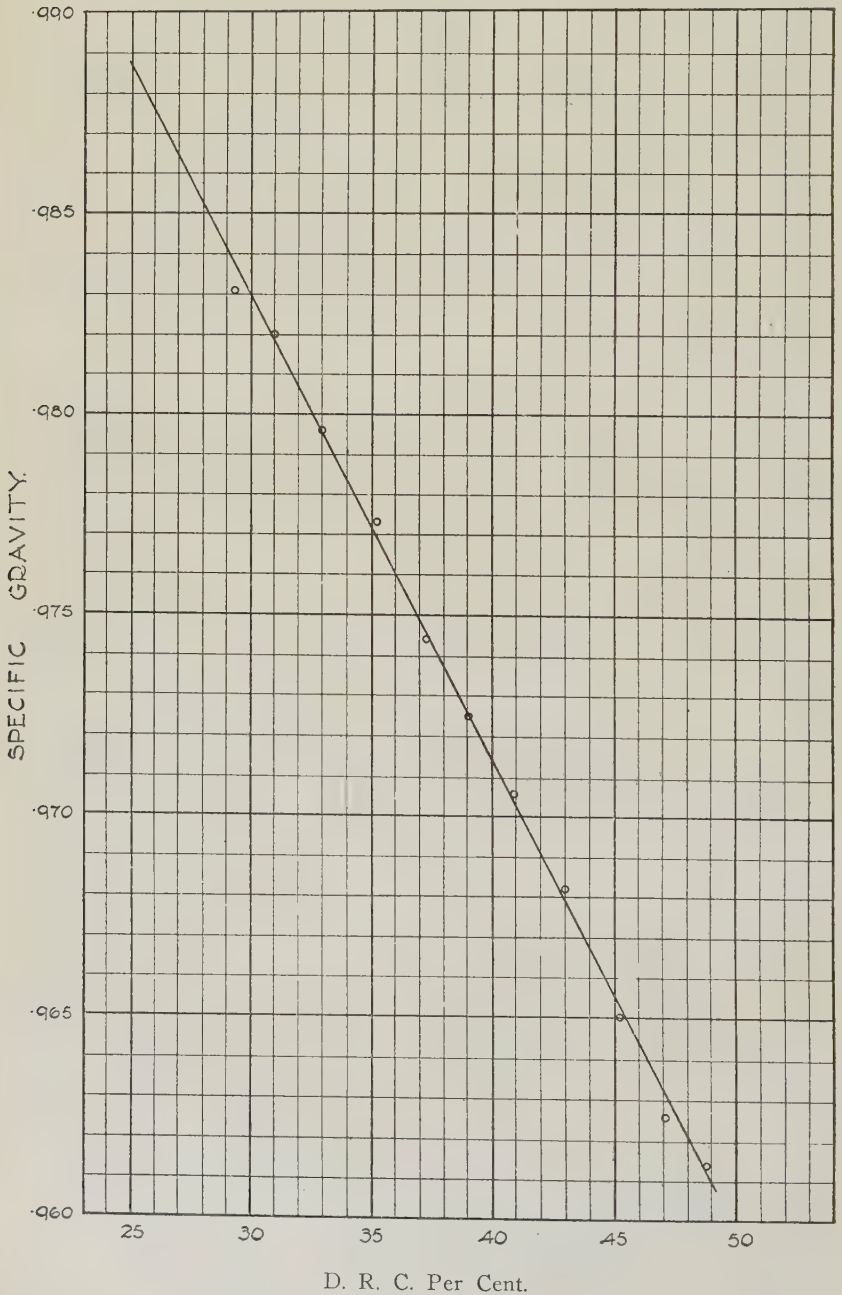
These calculations led to the broad conclusion that no great advantage could accrue from a multiplication of the already large number of observations and that, if the eleven values in columns 4 and 5 of Table II for mean dry rubber content and mean specific gravity were plotted, the most probable line through these points would have significance.

It is common in the preparation of a graph to plot the various points and to decide by simple visual inspection the position of the line or curve which best fits them. In the work of Scholtz and Klotz the position of the most probable line was decided by plotting each of the 85 individual experimental points and drawing a line by inspection more or less centrally through the rather widely-scattered point mass. The line so obtained for a range of dry rubber contents of 28 to 56 per cent. was then extrapolated in one direction to 100 per cent. rubber, so that in other words, the extrapolation zone in one direction was much greater than the experimental zone itself. A very slight error in the slope of the line in the experimental zone, must lead to a considerably magnified error in the deduced value for the specific gravity of the rubber disperse phase. Extensive extrapolation can in any case be criticised on many grounds, but where, as in this case, it is unavoidable, it is obviously important to fix the position of the experimental line not by simple visual inspection and personal judgment, but by mathematical calculation. The criticism that the investigator might have chosen by inspection a slightly different but apparently equally satisfactory line through the experimental points, and so obtained a different value at the extrapolation limit, can only be avoided if the position of the most probable line is determined mathematically.

In the present work the 852 values had been reduced, by the initial grouping, to the eleven mean points set out in columns 4 and 5 of Table II, and it had been shown that each of the mean points had statistical significance. They lie nearly on a straight line (see Fig. I) and, although the difficulty of fixing by inspection the line which best fits them is thereby rendered much less than in the case of Scholtz and Klotz, whose experimental points were ungrouped and therefore widely scattered,

FIGURE 1.

Specific Gravity and Dry Rubber Content of Preserved Latex.



it was decided to calculate the position of the line which best satisfied the eleven points.

The equation of the most probable line through the eleven mean points was calculated by the application of the "theorem of least squares" described by Feldman (5). It is required to calculate the most probable values of "m" and "b" in the equation

$$s = mt + b$$

where s = specific gravity and t = dry rubber content. The value for "m" is given by the equation

$$m = \frac{\Sigma t \times \Sigma s - n \Sigma (st)}{(\Sigma t)^2 - n \Sigma t^2}$$

and the value for "b" by

$$b = \frac{\Sigma t \times \Sigma (st) - \Sigma t^2 \times \Sigma s}{(\Sigma t)^2 - n \Sigma t^2}$$

where n = number of specific gravity—dry rubber content pairs.

Table III shows the arithmetical operations from which the values of "m" and "b" were derived by simple algebraical substitution in the above equations.

TABLE III

Mean D.R.C. (t)	(t^2)	Mean Specific Gravity (s)	(st)
29.3	858.49	.9831	28.80483
31.0	961.00	.9820	30.44200
33.0	1089.00	.9796	32.32680
35.2	1239.04	.9773	34.40096
37.3	1391.29	.9744	36.34512
39.1	1528.81	.9725	38.02475
40.9	1672.81	.9706	39.69754
43.0	1849.00	.9682	41.63260
45.2	2043.04	.9650	43.61800
47.1	2218.41	.9626	45.33846
48.8	2381.44	.9614	46.91632
$\Sigma t = 429.9$	$\Sigma t^2 = 17232.33$	$\Sigma s = 10.6967$	$\Sigma (st) = 417.54738$
$n = 11$			

The values derived for m and b are as under:—

$$m = -0.001158$$

$$b = 1.0177$$

and the equation of the most probable specific gravity—dry rubber content line, is thus

$$s = -0.001158\,t + 1.0177.$$

From this one may calculate the specific gravity "s" for any known dry rubber content "t" and, by calculating the specific gravity for each of the eleven dry rubber content means and comparing it with the experimental specific gravity mean itself, a picture is obtained of the closeness of approach of the experimental points to the line which represents them most fairly as a group. Table IV presents this comparison.

TABLE IV

Closeness of Approach of the Group-mean Points to the Line $s = -0.001158t + 1.0177$

1	2	3	4
Mean D.R.C.	Mean S.G. Experimental	S.G. Calc.	Deviation from experimental Group mean Specific Gravity
29.3	0.9831	0.9838	+ 0.0007
31.0	0.9820	0.9818	— 0.0002
33.0	0.9796	0.9795	— 0.0001
35.2	0.9773	0.9769	— 0.0004
37.3	0.9744	0.9745	+ 0.0001
39.1	0.9725	0.9724	— 0.0001
40.9	0.9706	0.9703	— 0.0003
43.0	0.9682	0.9679	— 0.0003
45.2	0.9650	0.9654	+ 0.0004
47.1	0.9626	0.9632	+ 0.0006
48.8	0.9614	0.9612	— 0.0002

It is observed that, at nine of the eleven dry rubber content values, the closeness of the specific gravity group-mean to the value shown by the line itself is 0.0004 or less. In Fig. 1, this is demonstrated graphically.

It will be remembered that, in the initial mathematical treatment, standard deviations of specific gravity were calculated about the mean specific gravity for a group which covered two units of dry rubber content. Within that group the deviation of all individual specific gravities were computed from the mean

specific gravity for that group without regard to the dry rubber content associated with the specific gravity of any particular individual in the group. The variation of specific gravity with dry rubber content within groups was not taken fully into account. It remained therefore to make certain that the dispersion of individual values within any group *about their own section of the chosen line* was not distinctly greater than that already derived about the single point which represents the group-mean specific gravity. It was necessary to compute the deviation of every experimental specific gravity value within a group from the specific gravity indicated by the line at the exact dry rubber content of that sample. Specific gravities were calculated along the chosen line at intervals of 0.1 units of dry rubber content over the whole experimental range. The individual experimental specific gravities within each group were then related to the calculated specific gravity at their respective dry rubber contents. In this way it was possible to derive values for the standard deviation of group members about the line rather than about the group-mean point. The data so obtained are presented in columns 10 and 11 of Table II. When these values are compared with the corresponding values, in columns 6 and 7 respectively, for standard deviation about the group means, it is seen that for seven of the eleven groups the dispersion about the line is slightly less than that about the corresponding group-mean; in one group the degree of dispersion is the same about the line and group-mean, and in the remaining three groups, the dispersion about the line is slightly greater than that about the corresponding group-mean. This indicates that, taking into account the dry rubber content of each of the experimental points, the grouping of their specific gravities is better about the chosen line than about the specific gravity group-means, upon which the line is based; the line $s = -0.001158t + 1.0177$ was therefore accepted as representing the relation between specific gravity and dry rubber content in preserved latex. By determining the standard deviation of the whole of the 852 samples from the line (see Table II column 11 bottom) it may be concluded that, if a single sample only were available for test, the chances would be even that the specific gravity obtained would lie within $\pm$ 0.0010 of the value shown by the line at that dry rubber content.

It was now possible to prepare the desired table for specific gravity and dry rubber content and this is presented as Table V. In order to check the values of De Vries (1 & 2) and Scholtz and Klotz (3) for the specific gravity of the rubber disperse phase, extrapolated values up to 100 per cent. rubber content have been included in the table and it is seen that the results lead to a

TABLE V

Specific Gravity Table for normal preserved Latex

from the Line $s = -0.001158t + 1.0177$

D.R.C. (t)	S.G. (s)	lb. per gallon Water = 10 lb.	oz.
0	1.0177	—	—
10	1.0061	—	—
15	1.0003	—	—
20	0.9945	—	—
25	0.9887	2	7½
26	0.9875	2	9
27	0.9864	2	10½
28	**0.9853**	**2**	**12¼**
29	**0.9841**	**2**	**13¾**
30	**0.9830**	**2**	**15¼**
31	**0.9818**	**3**	**0¾**
32	**0 9806**	**3**	**2¼**
33	**0.9795**	**3**	**3¾**
34	**0.9783**	**3**	**5¼**
35	**0.9772**	**3**	**6¾**
36	**0.9760**	**3**	**8¼**
37	**0.9749**	**3**	**9¾**
38	**0.9737**	**3**	**11½**
39	**0.9725**	**3**	**12¾**
40	**0.9714**	**3**	**14¼**
41	**0.9702**	**3**	**15¾**
42	**0.9691**	**4**	**1**
43	**0.9679**	**4**	**2½**
44	**0.9667**	**4**	**4**
45	**0.9656**	**4**	**5½**
46	**0.9644**	**4**	**7**
47	**0.9633**	**4**	**8½**
48	**0.9621**	**4**	**10**
49	**0.9610**	**4**	**11¼**
50	**0.9598**	**4**	**12¾**
51	0.9586	4	14¼
52	0.9575	4	15¾
53	0.9563	5	1
54	0.9552	5	2½
55	0.9540	5	4
56	0.9529	5	5¼
57	0.9517	5	6¾
58	0.9505	5	8¼
59	0.9494	5	9½
60	0.9482	5	11
61	0.9471	5	12½
62	0.9459	5	13¾
65	0.9424	—	—
70	0.9366	—	—
75	0.9308	—	—
80	0.9251	—	—
90	0.9135	—	—
100	0.9019	—	—

The figures in lighter type are obtained by extrapolation beyond the experimental zone.

specific gravity for the rubber disperse phase of 0.9019 which is in good agreement with, and confirmatory of the value of 0.901 derived by Scholtz and Klotz for fresh latex. There is therefore some reason to believe that the value of 0.914 found by De Vries (*loc. cit.*) and the value of 0.912 derived by extrapolation from the Rubber Trade Association specific gravity table are high.

It has already been explained that all values for specific gravity and dry rubber content were determined on the various samples of preserved latex after thorough shaking to re-disperse insoluble heavy solids. It is also the fact that the values for dry rubber content were obtained of necessity by coagulation and the weight of the dry coagulum was taken as representing the rubber disperse phase. It is obvious that a dry rubber content obtained in this way, while quite satisfactory for commercial purposes, does not give a coagulum consisting simply and solely of pure caoutchouc in the strictly scientific sense. It is well known that, when preserved latex is allowed to stand, an appreciable amount of heavy solids settles out, and it would be expected that the specific gravity of a latex from which the solids had been allowed to settle, would be less than that shown by the same latex after thorough shaking. Similarly, where preserved latex has been subjected to simple centrifugal clarification which removes solids, not only would it be expected that the specific gravity of the clarified latex would be less than that of the original latex, but also that, in carrying out a determination of dry rubber content, the coagulum obtained might be more free from adventitious heavy non-rubber solids and thus more closely represent pure rubber (caoutchouc). It follows therefore that specific gravity—dry rubber content values for centrifugally clarified latex, and also for latex which has been concentrated centrifugally might be expected to lie a little below those for preserved latex, and to lead to a specific gravity for the rubber disperse phase itself, which might be slightly less than that derived from the examination of normal preserved latex. It was felt that, without entering upon a systematic study of centrifuged latices, a few observations might afford some additional confirmation of the indication that the values of 0.914 and 0.912 for the specific gravity of the rubber phase of latex are probably on the high side. Some additional experiments were therefore made and these are described in Section B which follows:—

Section B
Experimental

Specific gravity variations in normal preserved latex after simple gravitational settlement were obtained by drawing

samples from tappers' buckets, sieving, ammoniating and allowing to stand for 48 hours. After sludge deposition had taken place, a sample of the supernatant latex was carefully withdrawn and its specific gravity was determined. The test sample was then returned to the bulk and, after thorough shaking, the specific gravity was again determined. In Table VI results are presented for seven random samples drawn on two occasions from different tappers' buckets.

TABLE VI

Specific Gravity Variations caused in normal preserved Latex by a gravitational Settlement of 48 hours

Sample	Specific Gravity after usual shaking	Specific Gravity of supernatant Latex after deposition of Solids	Difference due to deposition of Solids
1	0.9761	0.9727	— 0.0034
2	0.9802	0.9770	— 0.0032
3	0.9740	0.9709	— 0.0031
4	0.9681	0.9634	— 0.0047
5	0.9670	0.9658	— 0.0012
6	0.9712	0.9692	— 0.0020
7	0.9685	0.9674	— 0.0011

It is seen from Table VI that the specific gravity differences obtained after settlement for 48 hours, while by no means uniform, can be appreciable and in some cases of the order of — 0.004.

It was next sought to obtain some information on the closeness of approach of specific gravities of centrifugal concentrates to those presented for normal preserved latex in Table V. Sixty eight samples of centrifugal concentrate, most of them supplied by courtesy of Dunlop Plantations Ltd., were examined for dry rubber content and specific gravity. The results were arranged in groups according to dry rubber content and the mean specific gravity and mean dry rubber content were calculated for each group. The values so obtained were then compared with the specific gravities indicated in Table V for normal preserved latex at the appropriate dry rubber contents. The data so obtained are presented in Table VII.

TABLE VII

Individual Samples of Centrifugal Concentrate

Group D.R.C.	No. of Samples examined	Mean D.R.C.	Mean S.G.	Deviation from Value for normal Latex (see Table IX)
1	2	3	4	5
56.1 — 58.0	6	57.2	0.9476	— 0.0039
58.1 — 59.0	10	58.6	0.9458	— 0.0040
59.1 — 60.0	21	59.6	0.9442	— 0.0045
60.1 — 61.0	31	60.4	0.9426	— 0.0052

It is seen that in each group the specific gravity lies as was expected below the corresponding value for normal latex. The extent of the deviation approximates to − 0.004 to − 0.005 from the value derived from Table V for normal latex, and is seen to be in general greater but of the same order as that observed in Table VI when normal preserved latices are allowed to deposit solids by settling. If the specific gravity values for centrifugal concentrate are related, not to the values set out in Table V, but to those obtained by extrapolation of the figures of the Rubber Trade Association, which are themselves similar to those of De Vries (1 & 2), the deviations are much greater than those obtained when normal preserved latex is allowed to settle and are of the order of − 0.01. The inference is therefore again possible that, in the higher zones of dry rubber content, the values of De Vries and the Rubber Trade Association are high.

Further confirmation was next sought in a somewhat different manner. A single small bulk of latex was centrifuged and the skim latex and centrifugal concentrate from it were collected separately. By mixing the skim and cream fractions in varying proportions, clarified latices were obtained having dry rubber contents over a range from 16 to 57 per cent. approximately, and specific gravity and dry rubber content values were obtained over this range. The results are set out in Table VIII.

By the same procedure as that outlined in the calculation of the equation of the most probable line for normal latex, the equation of the line best representing the values in Table VIII was calculated. The equation was found to be $s = -0.001187t + 1.0153$, and from it a dry rubber content—specific gravity relationship can be calculated and compared with that set out

in Table V for normal latex. This comparison is made in Table IX.

TABLE VIII

Specific Gravity and Dry Rubber Content of Mixtures of centrifugal Concentrate and skim Latex from a single parent Latex

D.R.C. t	S.G. s
56.7	0.9480
55.2	0.9497
54.0	0.9513
52.7	0.9523
51.0	0.9548
48.1	0.9582
45.0	0.9626
41.1	0.9668
37.4	0.9705
34.2	0.9743
30.5	0.9788
23.5	0.9870
19.6	0.9922
15.7	0.9970

TABLE IX

Specific Gravity of a single Series of skim-concentrate Mixtures compared with Specific Gravities for normal preserved Latex

D.R.C.	Centrifugal Cream-Skim Mixtures	Specific Gravity of normal preserved Latex	Deviation from Specific Gravity of normal preserved Latex
35	0.9738	0.9772	— 0.0034
40	0.9678	0.9714	— 0.0036
50	0.9559	0.9598	— 0.0039
55	0.9500	0.9540	— 0.0040
56	0.9488	0.9529	— 0.0041
57	0.9476	0.9517	— 0.0041
57.2	0.9474	0.9515	— 0.0041
58	0.9465	0.9505	— 0.0040
58.6	0.9457	0.9498	— 0.0041
59	0.9453	0.9494	— 0.0041
59.6	0.9446	0.9487	— 0.0041
60	0.9441	0.9482	— 0.0041
60.4	0.9436	0.9478	— 0.0042
61	0.9429	0.9471	— 0.0042
62	0.9417	0.9459	— 0.0042
65	0.9381	0.9424	— 0.0043
80	0.9203	0.9251	— 0.0048
100	0.8966	0.9019	— 0.0053

Little or no importance can be attached to the fact that the deviations of the specific gravities of the artificial clarified latices, from those for normal preserved latices, are throughout the whole dry rubber content range of Table IX of the same order as the deviations shown by the 68 individual samples of centrifuged latex in Table VII; it must be remembered that the whole series of skim-cream mixtures represents only one single parent latex and that, by virtue of inherent differences in the specific gravity of the serum phase, different parent latices must yield slightly different lines for the skim-cream mixtures derived from them. The fact that, in this particular instance, the deviations at various dry rubber content values are all of the right order, amounts in all probability to little more than a coincidence. Some importance may however reasonably be attached to the single value for the specific gravity of the rubber phase at a dry rubber content of 100 per cent. because, while skim-cream mixtures derived from different parent latices would be expected to give lines of slightly different slope, these lines would all be expected to give approximately the same value for specific gravity at dry rubber content of 100 per cent. This figure is therefore one upon which comparison may be made with that obtained for normal latex. The value actually derived is seen from Table IX to be 0.8966 which deviates by − 0.0053 from the value of 0.9019 found in the present work for the rubber disperse phase in normal preserved latex. This deviation is again of the same order as those presented in Tables VI and VII but, if the value of De Vries and that derived from the Rubber Trade Association table for the specific gravity of the rubber disperse phase had been taken as the criterion from which to judge the deviation, it would then have been of the order of − 0.017 which is much greater than would be expected from the experiments which are summarised in Table VI. These results lead also to the inference that a value of the order of 0.912 − 0.914 for the specific gravity of the rubber disperse phase in preserved latex is probably high.

Discussion and Summary

A specific gravity—dry rubber content table (Table V) has been obtained from the examination of a large number of samples of preserved latex. This table differs slightly from that adopted by the Rubber Trade Association, London.

A value of approximately 0.902 has been derived for the specific gravity of the rubber disperse phase in normal preserved latex and this value is in good agreement with the value of 0.901 obtained by Scholtz and Klotz (3) working with fresh latex.

Experiments with individual samples of commercial centrifugal concentrate have indicated that, as a result of the removal of heavy solids, specific gravities of centrifugal concentrates may be expected to lie from 0.004 to 0.005 below the corresponding values for normal preserved latex.

Preliminary experiments with mixtures of the centrifugal concentrate and the skim latex obtained from a single parent latex have indicated that the value for the specific gravity of the true rubber phase in latex probably lies even below the value of 0.902 deduced from the examination of normal preserved latex.

Acknowledgments

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THE PROPERTIES OF CLONE RUBBER

PART II

BY

J. L. WILTSHIRE

In Part I of this series (1) an account was given of the day-to-day variations in the vulcanising properties of rubber from four clones over a period of six months. In the present communication are recorded observations on monthly average samples extending over a further period of two years from February 1932 to January 1934.

It is desirable, first, to discuss the objects and the limitations of these experiments. In the last few years it has frequently been suggested that rubber obtained from an individual clone might possess characteristic properties and that the differences in the properties of rubber from various clones might well be considerably greater than the variations in the properties of rubber from a mixed population of seedlings. A complete investigation of this problem must obviously extend over many years and, as mentioned in the previous paper, is handicapped, at present, by the difficulty of obtaining authentic samples from clones of proved commercial value. The present experiments therefore represent an attempt to obtain some information from the scanty material available. Their limitations lie mainly in the facts that none of the four clones studied can be regarded as more than moderate in commercial performance, and that the number of trees in each plot is small. A further limitation is that it is impossible to carry out a complete examination of the large number of samples involved and hence, for the majority of samples, only one figure can be reported. In the previous paper the vulcanising properties of a rubber-sulphur (100 : 10) mix of each sample were described only by a figure for a tensile modulus, i.e. the load required to give a fixed elongation after a fixed time of cure. The same method has now been used for monthly average samples over a period of two years. The previous publication was criticised, quite fairly, on the grounds that the tensile modulus method, while permitting comparisons within the series of samples, did not express the vulcanising properties in commonly understood terms. In the present paper

an attempt is made to remedy this defect in two ways, (a) a graph has been constructed, from observed figures, showing the times of cure which normally correspond to the different values of the modulus, (b) for one month's samples an extended range of cures has been carried out on each sample and figures have been obtained for tensile strength and for the time of cure giving the maximum tensile strength. The accuracy of these two series of figures will be discussed under the appropriate headings.

Survey of Literature

At an early stage in this investigation it became obvious that the variations in the rubber of each individual clone were at least as important, and probably more important, than any constant and characteristic differences between the clones. It will be necessary then, in discussing the results, to refer to information already available on the variation of vulcanising properties and a brief summary is given below.

The literature of "variability" is considerable but the greater proportion of the experimental work has been directed towards the variability arising from the treatment of the latex after it leaves the tree. This work has been carried out mainly by Eaton and his collaborators in Malaya (2, 3 and 4) and de Vries and his collaborators in Java (5). As a result of the researches of these two schools there is a fairly complete understanding of the influence of methods of preparation of raw rubber on vulcanising properties. The various factors concerned have been discussed at length by Whitby (6), de Vries (5) and Luff (7).

In the present experiments efforts have been made to eliminate variations in properties arising from variations in treatment in order to restrict attention to the behaviour of the plant itself. It cannot be claimed that the method of preparation of the rubber employed is absolutely uniform but everything possible has been done in this direction and there are no *known* variations in method of preparation to which variation in properties can be ascribed. The literature survey will therefore be confined to a consideration of the factors which may operate in and on the tree before latex is collected from the cups.

These factors were considered at length by de Vries and Whitby in their respective books (5, 6) both of which were published in 1920. Since both authors covered the same ground, their views are considered here jointly.

Season

The variation due to seasonal factors alone is considered to be small. During a drought (or the dry monsoon period in Java)

a low tensile strength is recorded and it is thought that this might be due to the combined influence of drought and wintering. This slight seasonal influence becomes more marked when trees are being very heavily tapped. There is no evidence of seasonal variation in rate of cure but the effect of wintering on very young trees remains to be investigated. Rainfall on any individual day did not appear to affect rate of cure.

Strain of Seed

It is stressed that differences between individual trees may be hereditary.

Age of Trees

There is a tendency for older trees to give a slow-curing rubber. The differences observed are, in general, quite small but one of de Vries' tables (Table I) suggests that during the first few years of tapping an appreciable slowing-down of cure may occur:

TABLE I

Area	Age	Time of cure
1	11 years	100 minutes
2	8 „	95 „
3	7 „	95 „
4	7 „	90 „
5	6 „	80 „

Height of tapping-cut

Within the ordinary tapping-panel only small differences are observed in rubber from latex collected at different heights. In some experiments, with two super-imposed cuts on the same tree, the rubber from the higher cut had a slightly higher rate of cure.

Tapping-system

In general the more drastic systems tend to give a latex of lower dry rubber content and a fast-curing rubber. This result is obtained, for instance, by very long cuts, very deep tapping or by the use of a large number of cuts on one tree. Very shallow tapping results in a latex of high D.R.C. and a slow-curing rubber. The tensile strength is not affected, except by very heavy tapping which may result in a slight fall.

Opening of new tapping-cut

When a tree is re-opened after a rest period, the D.R.C. is initially high and then drops to an equilibrium level. Similarly the rubber initially is slow-curing but speeds-up over a period of two to four weeks and then attains equilibrium. This is well illustrated by some figures given by de Vries (Table II):

TABLE II

	D.R.C. of latex per cent	Time of Cure of Crepe Minutes
2nd day	44.0	145
3rd „	39.4	145
6th „	35.0	140
9th „	33.8	135
13th „	30.4	125
16th „	29.6	115
20th „	28.0	107
25th „	26.4	103
5th week	25.3	99
6th „	24.6	96
7th „	25.7	98

The opening of a new tapping-cut on trees that are being tapped continuously, i.e. the change to a new panel, does not have such marked effects as re-opening after a rest.

Whitby's Summary

A study of de Vries' results led Whitby to formulate the general rule that any stress in the tree which leads to an increase of the ratio of serum substances to rubber will also cause an increase in the rate of cure. It is clear that drastic tapping systems cause a decrease in D.R.C. and some earlier experiments of de Vries had shown that, no matter how widely the specific gravity of the latex may vary, the specific gravity of the serum remains almost constant. Hence, argues Whitby, the proportion of serum substances in latex does not show any important changes and a decrease in D.R.C. must represent an increase in the ratio of serum substance to rubber. The experimental results indicate that a fall in D.R.C. is usually accompanied by an increase in rate of cure and Whitby's rule therefore follows naturally.

Since the publication of these books by de Vries and Whitby in 1920 little further information has become available and this

little is, on the whole, confirmatory of the original views of these authors. In 1922 de Vries (8) showed that, from one block of trees, in regular tapping over fifteen months, the rubber showed an extreme variation in time of cure of 10 minutes from 105 to 115. The individual trees of the block, however, showed variations between 90 and 135 minutes. The same worker (9) confirmed the fast rate of cure of young trees of 3 to 4½ years and its decrease with increasing age. In 1923 de Vries and Spoon (10) showed that an area brought into tapping in March showed a decrease in time of cure during the first month from 155 to 125 minutes and then during the next twelve months a variation of only 9 minutes, between 110 and 119. These samples were all prepared in the form of crepe. Spoon (11) studied the effect of rest periods of different lengths and drew the following conclusions: (a) rest of one month or less does not cause appreciable differences in the inner properties, (b) a rest of six or eight weeks may, in some instances, cause an appreciable slowing-down in rate of cure on re-opening, (c) a rest of three or four months always results in a definite decrease in rate of cure which may persist for the first month or six weeks of tapping. Riebl (12) gives figures for increase in time of cure over a period of three years:—crepe, from 77 minutes to 93 minutes; smoked sheet from 45 minutes to 65 minutes.

In 1924 the Dutch workers in Java adopted a standard of normality for rate of cure and defined a normal sample in any series as one having a time of cure within 20 per cent of the mean value for that series and a uniform sample as having a time of cure within 10 per cent of the mean. In a large number of samples of sheet tested by de Vries (13) over the period 1921—23 it was found that 60 per cent were uniform as regards rate of cure and 90 per cent were normal. In 1929 Riebl (14) reported that 83 per cent of the sheet samples examined were uniform and 97 per cent were normal. The variations covered in these series include, of course, those arising from the considerable differences in factory technique which would be found amongst estates all over Java.

Some interesting figures appear in a recent paper by Behre (15). This investigator studied the problem of vulcanisation from the physico-chemical point of view, using as his material a series of crepe samples from Buitenzorg. Before shipment from the East these samples were vulcanised in a 92.5 : 7.5 rubber-sulphur mix by de Vries who found, over a period of two years, practically no fluctuations in time of cure. Behre, however, working in Germany on the same samples with a 90 : 10 rubber-sulphur mix found considerable variations as shown in the following table:

Month	Time of Cure minutes	Month	Time of Cure minutes
1927 July	120	1928 July	124
August	120	August	105
September	118	September	107
October	120	October	124
November	120	November	139
December	130	December	120
1928 January	126	1929 January	118
February	128	February	118
March	130	March	123
April	110		
May	123		
June	119		

There is a rapid increase in time of cure in December 1927 and a fall in April 1928; similarly, high values are shown in October and November 1928. Behre comments that "it is surprising that a wet season gives a latex which vulcanises more rapidly than does that of a dry season. It is probable that this depends on the proportion of water-soluble fatty acids since, in the wet season, when the latex contains more water, a greater part of the acids will diffuse out of the disperse phase". From experiments on five additional samples Behre concludes that the rate of vulcanisation of rubber is proportional to its nerve and to its content of natural and artificial accelerators and inversely proportional to the free fatty acid content.

The available data concerning the properties of rubber from budgrafted areas is very limited and appears to be confined to the work of de Vries and his colleagues.

The most important paper from the experimental view-point is that published by de Vries in 1924 (16). In this paper it is shown that the variation in the properties of the individual rubber yielded by ten buddings of the same clone is considerably less than that from ten individual seedlings. The extreme limits for time of cure for seedlings were about twice those for buddings, while the average deviation from the mean time of cure was three times as great for seedlings as for buddings. This indicates that experiments with a small number of trees are more reliable when dealing with budgrafted rubber than with seedling rubber.

In 1927 de Vries and Spoon (17) published an account of further experiments on clone rubber. They quote figures for samples from trees of clones A.V.R.O.S. 52 and A.V.R.O.S. 80 which were being tapped for the first time at just under

four years. These samples appeared to have properties characteristic of young, newly-tapped rubber. Further experiments were carried out on clones established in the Economic Gardens at Buitenzorg. Unfortunately, in most of these clones, only very few trees were available and only one of the groups consisted of as many as ten trees. In this group the time of cure varied between 100 and 110 minutes and six of the ten samples gave the same figure of 110 minutes. Similarly the ten figures for tensile strength varied only from 1.38 to 1.47 kilograms per sq. mm., the average deviation from the mean being only 0.02 kgs/sq.mm. Of the six clones studied, three gave rubber of normal properties, one gave a slow-curing rubber of otherwise normal properties and two gave rubber of definitely inferior properties, i.e. low tensile strength and high figure for "slope."

The experiments therefore gave indications of differences between rubber from various clones but were not sufficiently exhaustive to permit the conclusion that these differences were constant and characteristic.

Since the publication of that paper no authentic information has appeared concerning the properties of rubber from the well-known "proved" clones.

Experimental

Vulcanisation Technique

The technique adopted was the standard method used in this laboratory and described by Bishop and Fullerton in 1931 (18). The following extracts from their paper are relevant:

Mixing — The standard mixing consists of 20 grams of sulphur and 200 grams of rubber. Three such mixings are made from the sample and from each mixing four equal portions of 40 grams each are obtained for vulcanisation.

Curing — The mixings are kept for a period of 24 hours, after which they are cured in moulds in a steam autoclave at 149°C using a standard N. P. L. thermometer to control the temperature.

Method of Testing — 24 hours after vulcanisation two rings are cut from each portion of 40 grams by means of a Schopper ring-cutting machine (rotating knives) giving a ring of 3.80 mm. width. The average thickness of the ring is obtained by a Schopper thickness gauge applied to the uncut test-piece.

The rings are stretched to breaking-point on a Scott Rubber Testing Machine which records

automatically on a chart the stress-strain relationships of the sample.

Corresponding to each period of cure, six rings are tested and the average of six results is recorded.

Modulus This is the load in kilograms per square millimetre obtained at an elongation of 650 per cent at a cure of 80 minutes.

This gives a figure which is used to compare different samples. It is more accurate than the figure for tensile strength at break which is subject to a large experimental error.

Experimental Error The results recorded for modulus are used as criteria for classifying the rubber tested. The actual figures are subject to an experimental error not greater than ± 4 per cent.

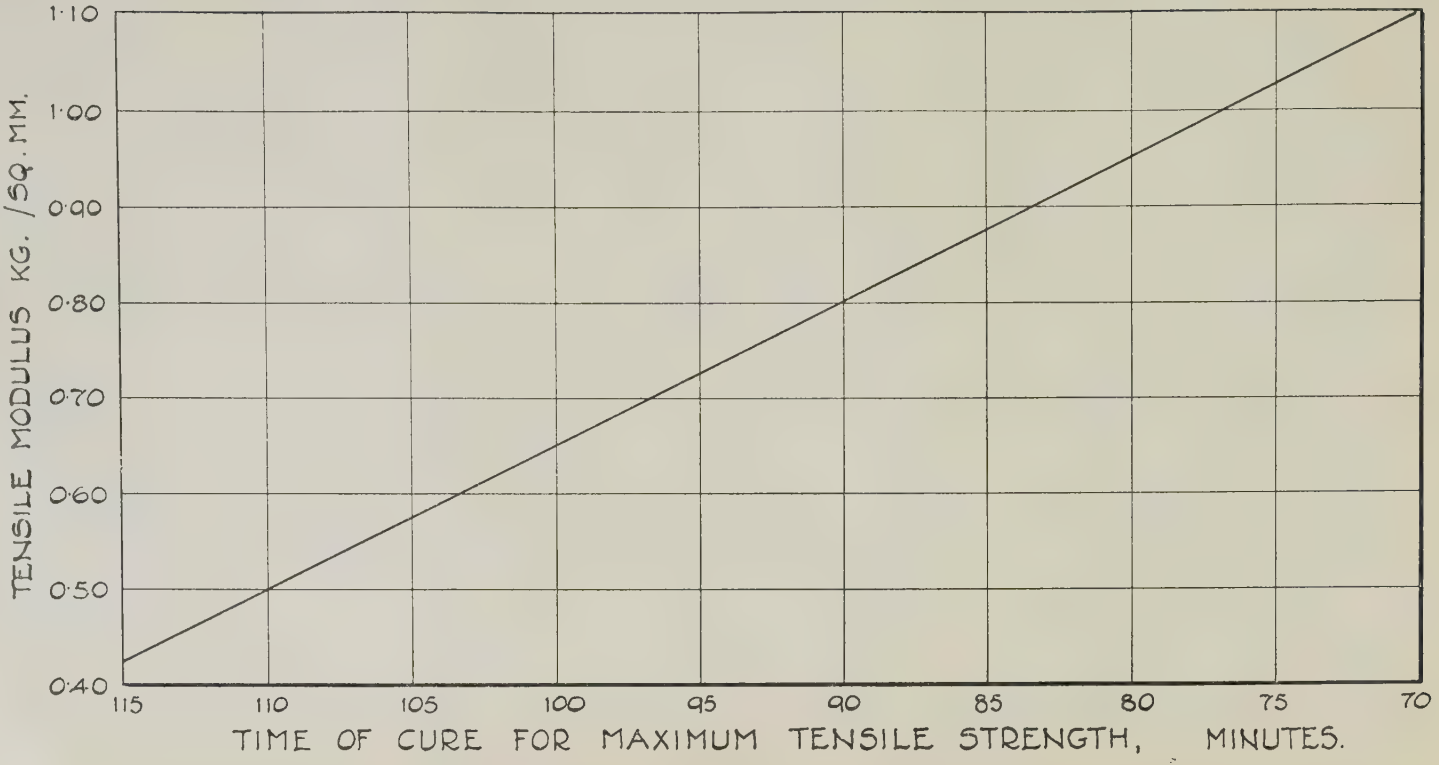
The details set out above need one correction. The machine used for testing is the Scott Tester which is normally used for dumb-bell test pieces. This particular machine has been adapted for rings, cut on a Schopper cutting machine, which are of different length from the Scott test pieces. Since it has been the practice to use the standard Scott graph-sheets the figures for elongation are incorrect and the so-called 650 per cent elongation actually represents an elongation of 825 per cent and a total length of 925 per cent. This correction, of course, in no way affects the accuracy of figures reported on this basis and merely implies that the arbitrarily-chosen reference line has been wrongly defined.

Interpretation of the Modulus as a Time of Cure

The present experiments have involved the determination of tensile modulus on 180 samples. Rather less than 100 of these have also been examined by an approximate method for time of cure giving maximum tensile strength. This method involves vulcanisations at four times of cure separated by 10 minutes each, testing two rings only at each time of cure and selection of the cure giving maximum tensile strength. This method is approximate only and it is not proposed to publish the results obtained. These results, however, have been used to select a reference point for the curve representing optimum cure. The criterion chosen was the load for a true elongation of 890 per cent (recorded on the Scott machine as 700 per cent). For each of the 92 samples examined this value was calculated for the cure giving maximum tensile strength. The mean value was 1.28 kg/sq. mm, with a co-efficient of variation of 4 per cent. As a convenient reference

FIGURE 1.

APPROXIMATE RELATION BETWEEN TENSILE MODULUS AND RATE OF CURE.



point for optimum cure it was therefore decided to adopt an elongation of 890 per cent and a load of 1.30 kg/sq. mm.

It was then possible to compare, for a large number of samples, the time of cure giving a curve passing through this point and the normal tensile modulus at 80 minutes' cure. From this comparison was constructed the straight-line graph reproduced in Figure 1. Within the range normally encountered it is considered that the use of this curve permits estimation, from the tensile modulus, of time of optimum cure to within five minutes of the time determined by experiment.

An example of the use of this curve is given in Table III which shows figures from 15 estate samples of smoked sheet. On each sample the tensile modulus at 80 minutes was first determined. Three further cures at five minute intervals were carried out, designed to give curves straddling the reference point and from these was selected the cure giving a curve closest to the reference point. This cure is regarded as the optimum

TABLE III

Sample no.	Tensile Modulus at 80 minutes Cure kg./sq.mm.	Predicted optimum Cure minutes	Determined optimum Cure minutes	Load at true Elongation of 890 per cent for optimum Cure kg./sq.mm.	Tensile Strength at optimum Cure kg./sq.mm.
1	0.55	105	105	1.28	1.29
2	0.45	115	115	1.31	1.33
3	0.46	110	110	1.32	1.39
4	0.56	105	100	1.28	1.46
5	0.60	105	105	1.29	1.34
6	0.71	95	90	1.34	1.42
7	0.48	110	110	1.30	1.31
8	0.46	110	115	1.26	1.29
9	0.43	115	110	1.30	1.38
10	0.50	110	105	1.29	1.33
11	0.53	110	105	1.37	1.42
12	0.66	100	95	1.37	1.42
13	0.46	110	105	1.27	1.36
14	0.67	100	95	1.35	1.51
15	0.41	115	115	1.33	1.37
Mean	0.53	108	105	1.31	1.37

and no further cures were carried out to give a curve passing *exactly* through the reference point as the general accuracy of the method does not justify the use of intervals of less than five minutes. The figure quoted for tensile strength is, in each instance, the mean result from four rings.

The accuracy of the graph was also tested on the clone rubber in a series of experiments in which the cure giving maximum tensile strength was actually determined by selection from a range of cures. Each sample was subjected to a range of five cures at five-minute intervals; eight rings were tested from each cure and the cure giving the highest average figure for tensile strength was selected. The results are given in Table IV, including the tensile moduli at 80 minutes' cure and the optimum cure predicted from the graph.

TABLE IV

Sample	Tensile Modulus for 80 minutes Cure	Predicted Optimum Cure	Determined Optimum Cure	Tensile Strength at Optimum Cure
August, 1933	kg./sq.mm.	minutes	minutes	kg./sq.mm.
Clone A 44, high panel ...	0.82	90	90	1.40
„ low panel ...	0.66	100	95	1.34
Clone B 16, high panel ...	0.54	110	110	1.50
„ low panel ...	0.53	110	110	1.40
Clone B 58, high panel ...	0.59	105	110	1.48
„ low panel ...	0.62	100	100	1.48
Clone B 84, high panel ...	0.84	85	85	1.40
„ low panel ...	0.71	95	100	1.51
Clone D 61, high panel ...	0.65	100	95	1.45
Clone D 65, high panel ...	0.55	105	110	1.48
Seedling block ...	0.58	105	110	1.46
Mean	0.64	100	101	1.45

It will be seen that, in this series, as in the preceding series, the observed cure never differs by more than five minutes from that predicted from the tensile modulus at 80 minutes' cure. The graph may therefore be regarded as sufficiently accurate for all determinations carried out under the conditions specified.

If it is desired to compare the absolute value of these results with those obtained by other investigators two points must be considered:

(a) *Value for time of cure.*

Vulcanisations are carried out in an autoclave which has been in use in this laboratory since 1927 and, previously, in the Department of Agriculture since 1914. The temperature is, and always has been, measured by a thermometer placed in a pocket on the unlagged top of the autoclave. In other laboratories the thermometer is sometimes placed in a pocket in a steam-pipe at the point where the steam leaves the autoclave; in others again, vulcanisation is carried out in an oil-bath in which the thermometer is directly immersed. Recent experience indicates that the two latter methods give rather higher values for time of cure than the method used in this laboratory and the probable explanation is that the temperature of the vulcanising rubber under the latter conditions is appreciably higher than that of the pocket in the top of the autoclave. Times of cure for these samples determined on a 100 : 10 rubber-sulphur mixing at 149°C in an oil-bath would probably be about 15 minutes longer than those determined under present conditions.

(b) *Value for tensile Strength.*

Reference has already been made to the somewhat hybrid apparatus used for testing, i.e. a Scott machine stretching "Schopper" rings. Comparison with results obtained in other laboratories has shown that the values for tensile strength thus obtained are rather lower than those obtained from duplicate rings tested on a Schopper machine. To make this comparison a series of pieces of the standard mixing were vulcanised in this laboratory and two rings were cut from each piece, one of which was stretched on the Scott machine and the other on a Schopper machine in a commercial laboratory. This was repeated at several times of cure and a comparison of the average results for eight rings at each cure showed that the Schopper machine gave tensile strength figures about 20 per cent higher than those given by the Scott machine.

These two corrections apply to *all* vulcanisations carried out under the conditions specified but do not affect comparisons within the series. They arise from faults in the apparatus available and it is hoped that, with the installation of a new Schopper machine and an alteration in the method of recording temperature,

it will be possible in future to publish results more directly comparable with those of other investigators.

Details of the Trees and Field Methods

The bud-grafted trees from which samples were obtained are those of clones A. 44, B. 16, B. 58 and B. 84, established on Pilmoor Estate, Selangor. Their early history may be found in the Bulletins of the Rubber Growers' Association (19), Annual Reports of the Rubber Research Institute (20) and in a paper by Sanderson and Sutcliffe (21). Further yield records have recently been published in this Journal (22, 23 and 24) while a complete account of yield records over the first five years of tapping is in course of preparation by the Botanical Division. It should be pointed out that the trees are maintained and tapped for the purpose of obtaining botanical data and that sampling for chemical purposes is a secondary object. The method of tapping and other experimental details have therefore been controlled by the Botanical Division, although every facility has been given to the Chemical Division for the collection of samples and information.

The trees were planted as "stumped" buddings in December 1924 and were brought into test-tapping in January 1928 at the age of three years. The system of tapping during the period under review, and for some years previously, has been constant, viz. alternate-daily on a half-circumference left to right single-cut at an angle of 35° to the horizontal. The actual position of the tapping-panel has varied and the experiment has been so conducted as to yield a comparison of tapping on high and low cuts. For this purpose each clone was divided into two groups and changes were made as follows:

In February 1932 all the trees were being tapped on the original panels at an average height of 12 inches above the union of stock and scion. In May 1932, when about 8 inches of the original panel was still unused, each clone-block was divided into two groups. In group A tapping was continued on the original panel. In group B a new panel was opened at 40 inches above the union. This system continued until January 1933 and during this period of eight months there was a comparison between tapping on a high panel and on a low panel. In January 1933 the low panel of the trees of group A had been exhausted and they were accordingly opened on the new panel at 40 inches. Simultaneously, on the trees of group B, the unused portion of the original panel was re-opened. This latter panel was exhausted in September 1933 and, in October 1933, the trees of group B were

re-opened on the upper panel. These changes may be summarised thus:

	Group A	Group B
1932 February to April inclusive	Original panel at about 9 ins.	Original panel at about 9 ins.
1932 May to December inclusive	Original panel from 8 ins. down	New panel at 40 ins.
1933 January to September inclusive	New panel at 40 ins.	Original panel re-opened from 8 ins. down
1933 October to 1934 January	New panel at 32 ins.	New panel re-opened at about 32 ins.

The number of trees in each group decreased slightly during the period owing to unavoidable losses. The minimum number in tapping are as follows:

Clone	Group A	Group B	Total
A 44	20	15	35
B 16	18	18	36
B 58	15	15	30
B 84	8	8	16

For the greater portion of the period—until June 1933—Group B of clone A 44 consisted of 21 trees.

For the purpose of comparison samples were also taken from a neighbouring area of seedling rubber of about 112 acres. This rubber was planted in 1921 and is therefore some three years older than the clone rubber. The collection and treatment of the latex was carried out in the normal estate routine.

Preparation of the Samples

The collection of latex was carried out in the normal manner, no sodium sulphite or other anti-coagulant being used. The latex from each group of trees was bulked, diluted to a concentration of 1.5 pounds of rubber per gallon and coagulated in pans in one gallon batches with a standard quantity of formic acid. Coagula-

tion proceeded overnight, the coagulum was machined with a plentiful supply of water on the rolls, the wet sheet was dripped for five to six hours, and smoked in a period of four days.

The sample received at the Institute each month represented the whole of the crop from each group of trees and the sampling error was therefore restricted to that involved in selecting 600 grams of rubber from the 20 or 30 sheets representing the month's crop. The sheets were fairly uniform in size and the method employed was to stack them as evenly as possible, roll into a tight cylinder and cut transverse sections for vulcanisation.

An indication of the accuracy of this sampling method was obtained by performing all the determinations in duplicate on the rubber for December 1933. Each "single" determination, of course, was the average from three mixes, two rings from each mix being tested, as described in the standard method. The results are shown in Table V:

TABLE V

Duplicate Tensile Modulus Determinations
kg./sq.mm.

Sample	First Determination				Second Determination				Difference as percentage of Mean
	(i)	(ii)	(iii)	Mean	(i)	(ii)	(iii)	Mean	
A 44 (A)	0.66	0.66	0.66	0.66	0.61	0.62	0.63	0.62	6.2
(B)	0.57	0.57	0.58	0.57	0.62	0.62	0.65	0.63	10.0
B 16 (A)	0.58	0.58	0.60	0.59	0.55	0.54	0.54	0.54	8.8
(B)	0.57	0.58	0.58	0.58	0.57	0.56	0.58	0.57	1.7
B 58 (A)	0.62	0.63	0.64	0.63	0.61	0.60	0.59	0.60	4.9
(B)	0.63	0.64	0.62	0.63	0.65	0.66	0.65	0.65	3.1
B 84 (A)	0.71	0.71	0.70	0.71	0.66	0.66	0.65	0.66	7.3
(B)	0.73	0.72	0.71	0.72	0.77	0.76	0.77	0.77	6.7
									Mean 6.1

Thus the maximum difference between duplicate determinations is about ten per cent and the mean difference is six per cent. It has not been possible to carry out sufficient determinations on one sample to obtain a precise figure for the sampling error, but the above table indicates that a difference of more than 10 per cent. between the tensile moduli of two samples will, in general, be significant.

These remarks apply only to the clone rubber. The sample of seedling rubber tested each month was selected from the whole crop from that area and is therefore subject to a larger sampling error.

Discussion of Results

Comparison of high and low Tapping-Panels

The question to be decided in this section is whether the rubber from trees of the same clone tapped at different heights shows a significant difference in rate of cure which can be attributed to this difference in height. Samples from the two groups were not examined separately until September, 1932 and the period previous to this is therefore not considered. Table VI shows the tensile modulus figures for the samples from A and B groups, divided into periods corresponding to the changes in tapping-panel already described. The differences between corresponding A and B group samples are summarised in Table VI.A where differences between two figures greater than 10 per cent. of their mean are regarded as significant.

If difference in tapping-height is directly responsible for differences in rate of cure then Periods I and II, when A and B

TABLE VI

Tensile Modulus over two-year Period

All Figures in kg./sq.mm.

Period I September–December 1932, inclusive

Group A = Low Panel Group B = High Panel

1932	A 44		B 16		B 58		B 84		Mean	
	Group A	Group B	Group A	Group B	Group A	Group B	Group A	Group B	Group A	Group B
September	0.98	1.12	0.84	0.81	0.85	0.86	1.12	1.04	0.95	0.96
October	0.94	1.01	0.80	0.96	0.78	0.67	1.03	0.94	0.89	0.89
November	0.91	0.94	0.77	0.85	0.89	0.73	0.96	0.95	0.88	0.87
December	0.88	0.95	0.63	0.82	0.69	0.71	0.86	0.95	0.77	0.86
Mean	0.93	1.01	0.76	0.86	0.80	0.74	0.99	0.97	0.87	0.90

Period II January—September 1933, inclusive

Group A = High Panel Group B = Low Panel.

1933	A 44		B 16		B 58		B 84		Mean	
	Group A	Group B	Group A	Group B	Group A	Group B	Group A	Group B	Group A	Group B
January	0.54	0.67	0.66	0.66	0.62	0.63	0.65	0.87	0.62	0.71
February	0.59	0.68	0.51	0.67	0.58	0.56	0.70	0.74	0.59	0.66
March	0.68	0.83	0.64	0.72	0.63	0.60	0.65	0.72	0.66	0.72
April	0.60	0.74	0.57	0.59	0.51	0.61	0.61	0.52	0.57	0.62
May	0.50	0.64	0.49	0.47	0.53	0.50	0.63	0.55	0.54	0.54
June	0.58	0.69	0.52	0.53	0.60	0.52	0.60	0.67	0.58	0.63
July	0.78	0.83	0.57	0.62	0.63	0.75	0.76	0.79	0.69	0.75
August	0.82	0.66	0.54	0.53	0.59	0.62	0.76	0.71	0.68	0.63
September	0.52	0.59	0.51	0.48	0.58	0.58	0.57	0.70	0.55	0.59
Mean	0.62	0.70	0.56	0.59	0.59	0.61	0.66	0.70	0.61	0.65

Period III October 1933—January 1934, inclusive

Both Groups on high Panel

1933 1934	A 44		B 16		B 58		B 84		Mean	
	Group A	Group B	Group A	Group B	Group A	Group B	Group A	Group B	Group A	Group B
October	0.65	0.58	0.59	0.49	0.56	0.63	0.68	0.69	0.62	0.60
November	0.89	0.72	0.63	0.59	0.70	0.76	0.75	0.81	0.76	0.72
December	0.64	0.60	0.57	0.58	0.62	0.64	0.69	0.75	0.63	0.64
January	0.83	0.60	0.62	0.51	0.67	0.70	0.75	0.71	0.72	0.63
Mean	0.75	0.63	0.62	0.55	0.64	0.68	0.72	0.74	0.68	0.65

TABLE VI A

Differences between tensile Modulus Figures for high and low Panels

Symbols

O = no significant difference

In Periods I and II { H = high-panel value significantly greater
L = low-panel value significantly greater

In Period III S = significant difference between two panels at same height

1932	A 44	B 16	B 58	B 84
	Period I			
September	H	O	O	O
October	O	H	L	L
November	O	O	L	O
December	O	H	O	O

O, 10; H, 3; L, 3; Total 16

Significant differences represent 38 per cent. of total

1933	*Period II*			
January	L	O	O	L
February	L	L	O	O
March	L	L	O	L
April	L	O	L	H
May	L	O	O	H
June	L	O	O	L
July	L	O	L	O
August	H	O	O	L
September	O	O	O	O

O. 18; H, 3; L, 15; Total 36

Significant differences represent 50 per cent. of total

1933—1934	*Period III*			
October	S	S	S	O
November	S	S	O	O
December	O	O	O	O
January	S	S	O	O

O. 9; S, 7; Total 16

Significant differences represent 44 per cent of total

groups were in tapping at different heights, should disclose differences which disappear in Period III when both groups were tapped at the same height.

From Table VI the simplest test is a comparison of the mean values for A and B groups over the three separate periods. In Period I the high-panel group gives a mean value 0.03 units greater than the low-panel group. In Period II the low-panel group gives a mean value 0.04 units greater than the high-panel group. In Period III one group gives a value 0.03 units higher than the other, although they are both in tapping at the same height. There is therefore no constant and characteristic difference in mean values attributable to difference in tapping heights.

This conclusion is confirmed by Table VI.A which shows that significant differences occur no more frequently in Periods I and II than in Period III and there is no evidence that the significant differences that occur are due to differences in tapping height.

In Period I there are six significant differences—three in each direction. In Period II there are 18 significant differences and, on 15 of these 18 occasions, the low panel gives the larger figure. The tendency for this predominance lessens as the period progresses and is probably connected with the change of panel in January. The high panel here is newly opened, whereas the low panel is re-opened after eight months' rest. It has already been observed that the opening of a new cut tends to decrease the rate of cure (and the modulus) and it would be expected that the effect of an opening new cut would be greater than that of re-opening an old cut, i.e. that the high-panel figures would be depressed more than the low-panel figures. It will be observed in Table VI.A that, during the first four months of Period II when this difference would be most effective, eight of the sixteen comparisons show the low panel giving a significantly higher tensile modulus.

The mean values for each month have been plotted and are shown in Figure 2, the changes in tapping panel being shown by changes in colour. Apart from the depression of the high-panel values from January to April 1933 the two curves run very close together.

Thus, although the two groups sometimes show considerable differences in rate of cure, as indicated by tensile modulus, there is no evidence that these differences are associated with differences in the height of tapping.

TABLE VII

Tensile Modulus

Mean Values for Groups A and B over two-year Period
All figures in kg./sq.mm.

	A 44	B 16	B 58	B 84	Mean	Mean Deviation
1932 February	0.99	0.81	0.71	0.88	0.85	0.07
March	0.76	0.88	0.73	0.71	0.77	0.05
April	0.95	0.85	0.73	0.73	0.82	0.08
May	0.63	0.60	0.66	0.57	0.62	0.03
June	0.74	0.66	0.66	0.77	0.71	0.05
July	0.67	0.78	0.67	0.78	0.73	0.06
August	0.74	0.70	0.72	0.85	0.75	0.05
September	1.05	0.83	0.86	1.08	0.96	0.11
October	0.98	0.88	0.73	0.99	0.89	0.09
November	0.93	0.81	0.81	0.96	0.88	0.07
December	0.92	0.73	0.70	0.91	0.82	0.10
1933 January	0.61	0.66	0.63	0.76	0.67	0.05
February	0.64	0.59	0.57	0.72	0.63	0.05
March	0.76	0.68	0.62	0.69	0.69	0.04
April	0.67	0.58	0.56	0.57	0.60	0.04
May	0.57	0.48	0.52	0.59	0.54	0.04
June	0.64	0.53	0.61	0.64	0.61	0.04
July	0.81	0.60	0.69	0.78	0.72	0.08
August	0.74	0.54	0.61	0.74	0.66	0.08
September	0.56	0.50	0.58	0.64	0.57	0.04
October	0 62	0.54	0.60	0.69	0.61	0.04
November	0.81	0.64	0.73	0.78	0.74	0.06
December	0.62	0.57	0.63	0.72	0.64	0.05
1934 January	0.72	0.57	0.69	0.73	0.68	0.05
Mean	0.76	0.67	0.67	0.76	0.72	0.06
Standard deviation	0.14	0.12	0.08	0.13	0.11	—
Co-efficient of variation	18%	18%	12%	17%	15%	—
Extreme range	0.56—1.05	0.48—0.88	0.52—0.86	0.57—1.08	0.54—0.96	—
Extreme range of time of cure	105—75 (minutes)	110—85 (minutes)	110—85 (minutes)	105—70 (minutes)	105—80 (minutes)	—

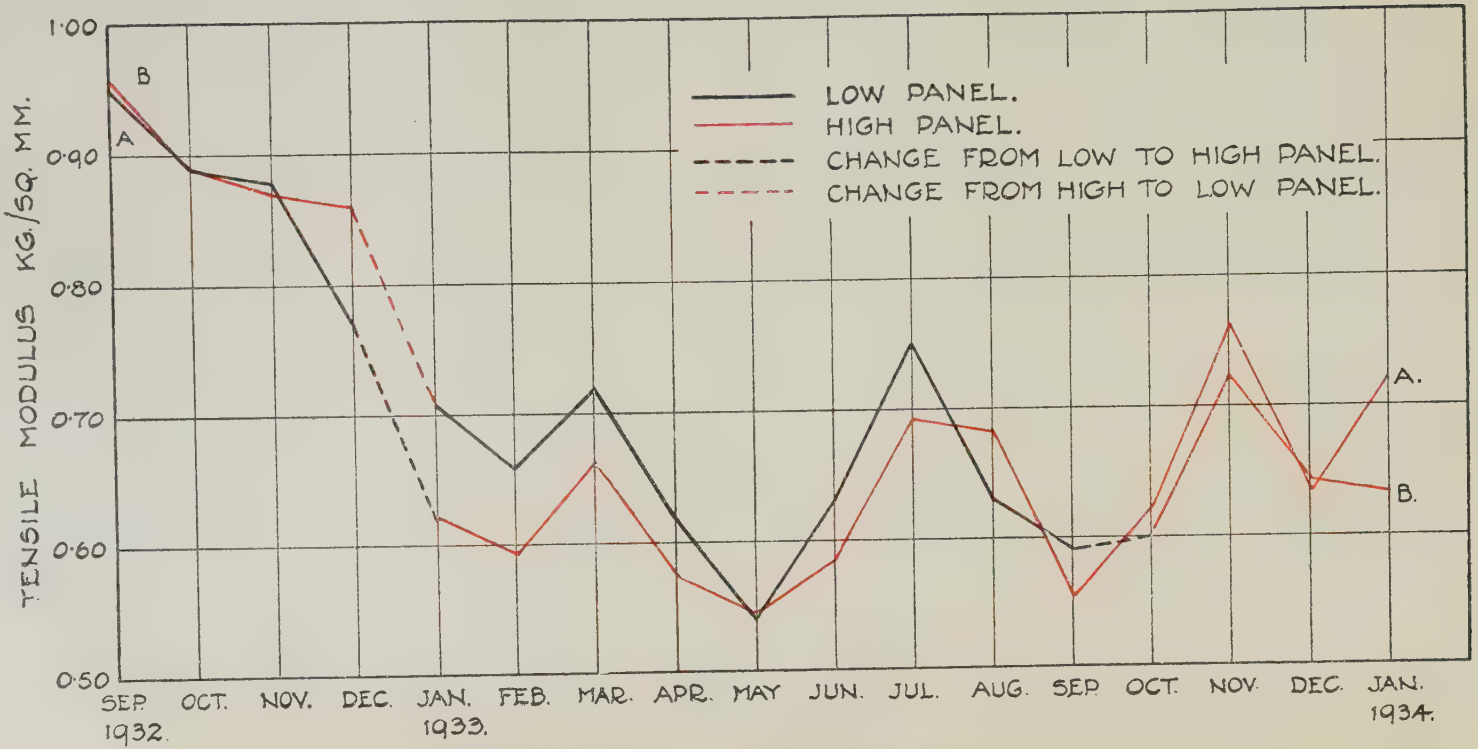
Comparison of the four clones

In view of the irregular differences between the A groups and the B groups it is considered that comparisons between the four clones are best made on the basis of average values of the two groups. These average values are shown in Table VII.

FIGURE 2.

COMPARISON OF A AND B GROUPS. (TABLE VI)

MEAN MONTHLY VALUES OF TENSILE MODULUS.



Considering first the four mean values for the two-year period it will be seen that the clones fall into two pairs. Rubber from clones A 44 and B 84 is faster-curing than that from clones B 16 and B 58. The difference in tensile modulus is 0.09 kg. per sq.mm. which is equivalent to 12.5 per cent of the general mean and must therefore be regarded as significant. In terms of time of cure this difference is equivalent to 6 minutes, i.e. between 99 minutes and 93 minutes.

The degree of variation within three of the clones is about equal but clone B 58 shows appreciably less variation than the other clones.

The variation between the four clones in each month, as measured by the mean deviation, is only about one-half the variation within each clone separately, as measured by the standard deviation. This indicates a certain degree of parallelism in the variations of the four clones and this parallelism is still more evident in Figure 3, which shows the variations in tensile modulus over the two-year period. A mathematical expression is given to this parallelism by the figures which have been calculated for the correlation co-efficients for the four series taken in pairs, viz:—

B 16 — B 84	0.71
B 58 — B 84	0.78
A 44 — B 58	0.78
B 16 — B 58	0.82
A 44 — B 84	0.82
A 44 — B 16	0.85

For the correlation of two series each containing 24 figures, a co-efficient of 0.52 corresponds to a significance of 0.01, i.e. it may occur on one per cent of occasions as a matter of chance. All the above correlation co-efficients therefore represent a very high level of significance.

Seasonal Variation

Reference to Part I of this series (1) will show that daily variations over a period of six months also shewed considerable parallelism, although the correlation co-efficients were lower than in the present instance. It was then suggested that the variations in rate of cure were controlled by factors external to the tree and that these factors acted similarly and simultaneously on all the trees in the area. Certain suggestions were also made as to

the nature of these factors and, of the possibilities advanced, four were climatic, i.e. temperature, sunlight, rainfall and soil conditions, and two were connected with tapping, i.e. small variations in time and in method. The considerable changes which have now been observed from month to month show that fortuitous differences in tapping are not a controlling factor since these must be expected to average out and to have no effect in a monthly average sample. The variations are almost certainly seasonal and their cause must be looked for in climatic changes or, a factor which was previously overlooked, in physiological changes in the tree. The latter are, to some extent, connected with climatic variation but some botanical observers hold that the tree has an inherent rhythm of its own which is influenced but not completely controlled by climatic variation. The question has been discussed at length by Schweizer (25). It would perhaps be surprising if four distinct clones corresponded in their rhythm to the extent that the four tensile modulus curves correspond, but it is a possibility that cannot be rejected.

In the present experiments the problem of the cause of these variations in rate of cure has by no means been solved. From the information available it has not even been possible to advance a convincing or generally applicable hypothesis, as the following discussion will show. As a preface to this discussion it is pertinent to remark that there is no basis for the supposition that a rise in rate of cure observed at one particular time is due to the same cause as a rise in rate of cure at a different time of year.

Variations in rate of cure must be regarded fundamentally as a result of variations in composition of the latex. These latter variations may affect the caoutchouc itself, the accessory substances, or both. The question of the constancy of constitution of caoutchouc has received very little attention, owing to the great experimental difficulties. There is apparently no evidence to show that the caoutchouc molecule is always of the same size and structure and it may be subject to variations which would affect the velocity of the vulcanisation reaction. From general considerations it is not unlikely that variations of the conditions under which caoutchouc is synthesised in the tree should be reflected in small variations in the structure of the molecule and hence in its chemical and physical properties.

The influence of the non-caoutchouc substances on rate of cure has been studied more thoroughly and most investigators agree that, in general, higher contents of these substances are associated with higher rates of cure. Whitby (6) has formulated the general rule that any factors tending to increase the ratio of serum substances to caoutchouc in the latex also tend to increase the rate of cure.

FIGURE 3

TENSILE MODULUS OVER TWO YEARS.

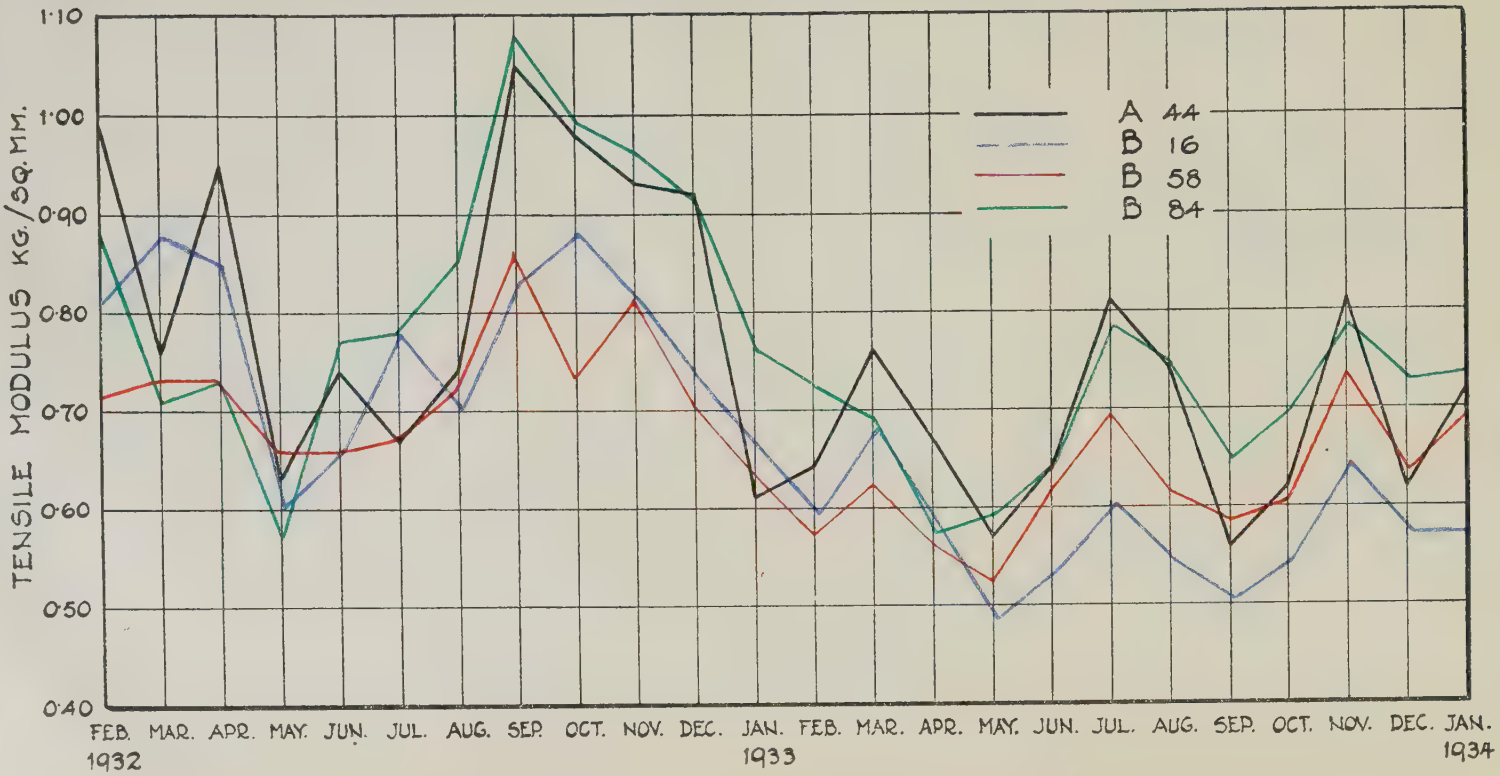
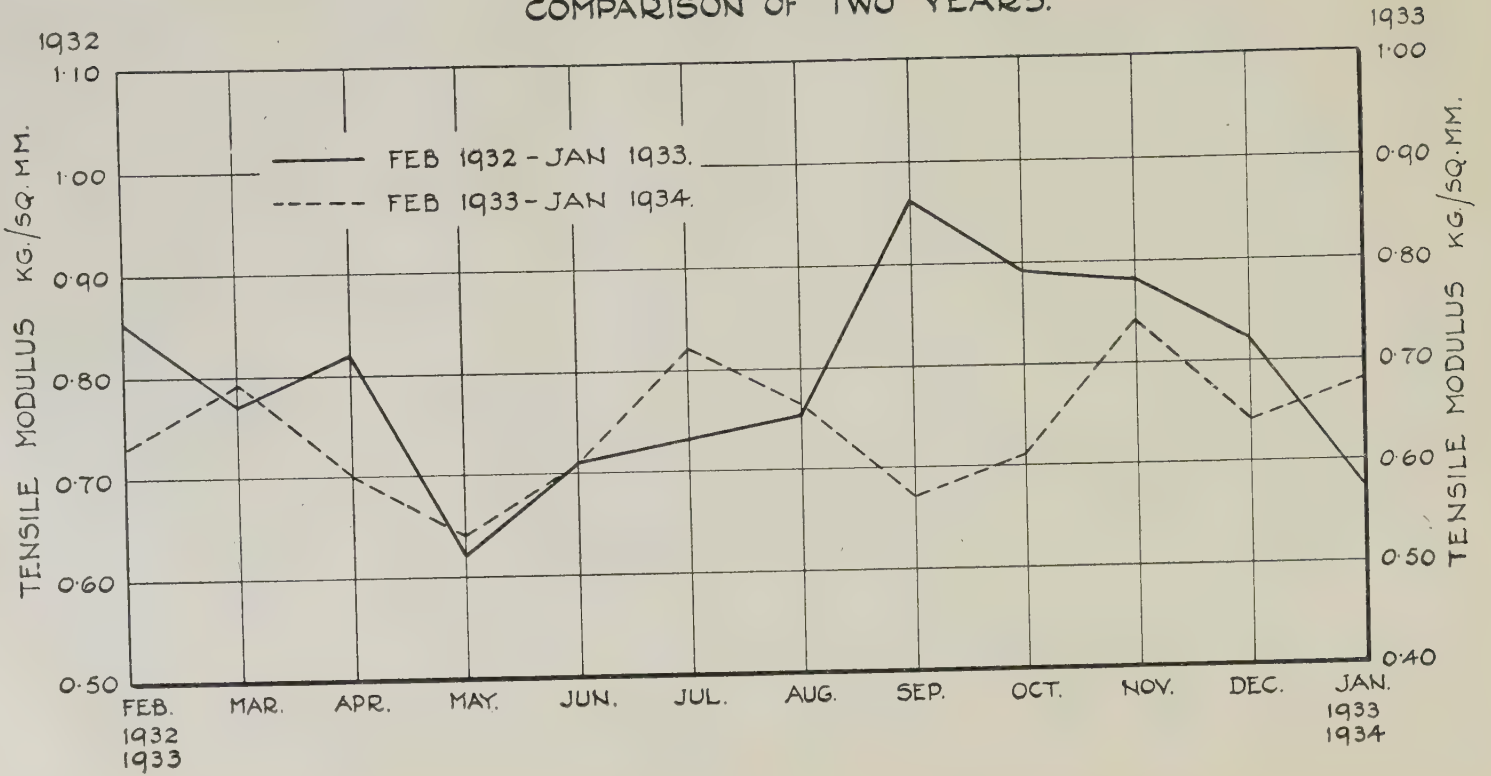


FIGURE 4 TENSILE MODULUS - AVERAGE OF FOUR CLONES.

COMPARISON OF TWO YEARS.



Eaton and Grantham showed that the greatest effect on rate of cure was effected by the maturation of the coagulum and indicated that this was due to the decomposition of the protein in the latex or in the serum remaining in the coagulum and the probable formation of nitrogenous bases from the proteins which act as accelerators of vulcanisation.

They showed also that "whole" rubber prepared from latex by drying of thin films, in order to retain all the serum constituents, gave a product with a rapid rate of cure, although in this case, the increase in rate of cure could not be associated with "maturation" or changes in the coagulum and must be due to "natural accelerators" present in the latex in the tree.

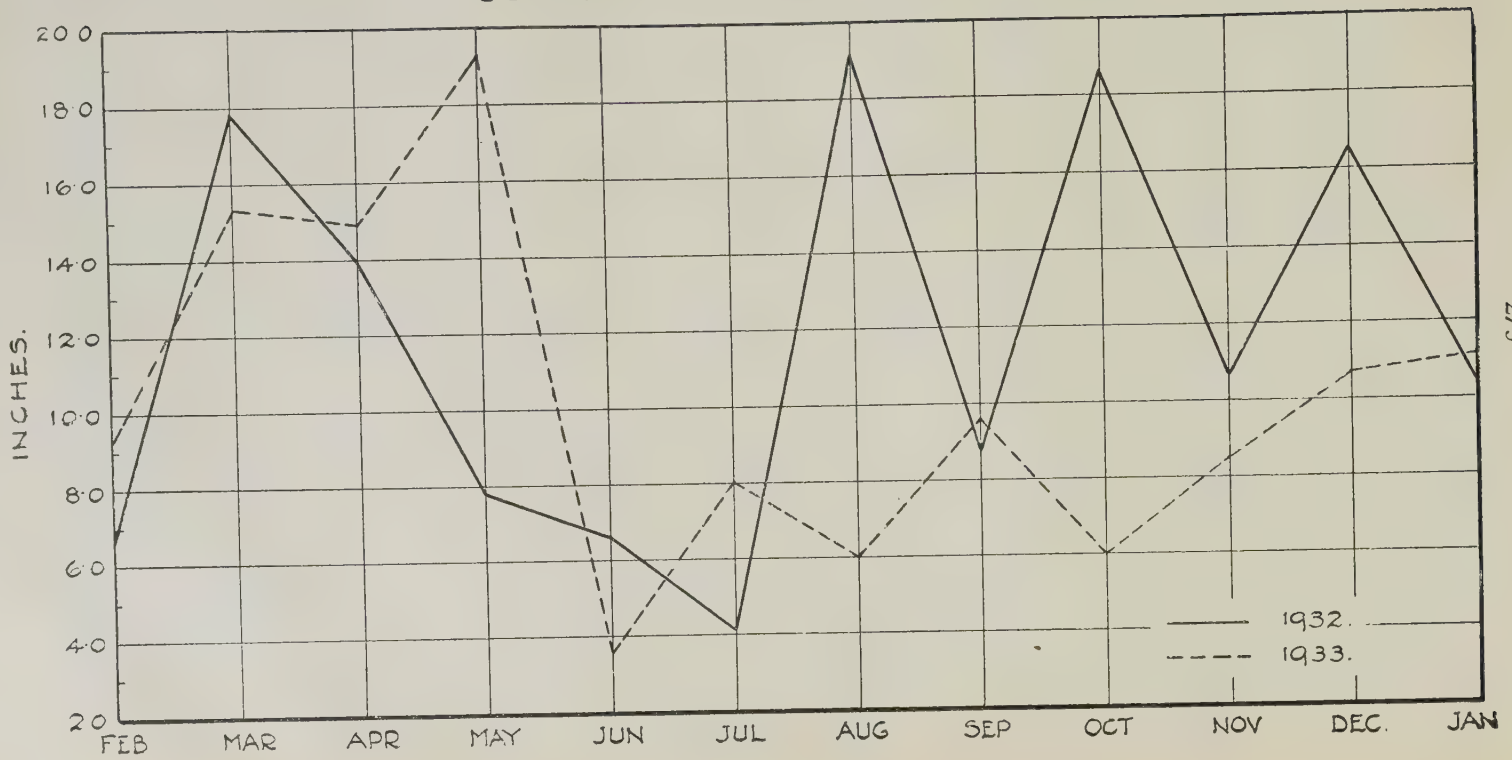
Subsequently Stevens (26) showed that the increase in rate of cure was due to nitrogenous bases formed during putrefaction and later Bruni (27) isolated tetra- and pentamethylene diamines and potassium phenylacetate, all of which are powerful accelerators. If no directly opposing factors are present the rate of cure should vary with the content of these specific natural accelerators. It will vary with the *total* non-rubber content in so far as this is proportional to the content of accelerators. It is unlikely that the proportion of accelerators to non-rubbers would remain constant and therefore Whitby's rule is unlikely to be more than a very rough guide. A further possibility is the presence of other compounds possessed of a retarding effect. It will be remembered that Behre (15) suggested that the faster cures observed by him in wet months of the year were due to the comparatively low amounts of fatty acids associated with the caoutchouc particles of the latex. This particular suggestion will be discussed more fully in the next part of this series.

The nature of the variations under discussion and their relation to season is best seen in Figure 4. Here the average values for tensile modulus of the four clones are plotted separately for the two twelve-month periods. The first and most obvious feature of a comparison of the two years is that the 1933 figures are consistently lower than the 1932 figures. The most probable explanation of this fact is that the increasing age of the trees is causing a steady decrease in rate of cure (see de Vries, 5). The truth of this statement cannot be proved but it is a reasonable assumption supported by the findings of earlier investigators. This general difference in level is therefore eliminated from the discussion and, in the figure, the 1933 figures are plotted 0.10 unit higher than the 1932 figures. The curves thus obtained show both similarities and divergences. In each year there is a definite minimum in May followed by a rise until July. In 1932 this rise is continued to a maximum in September and then a

FIGURE 5

RAINFALL

COMPARISON OF TWO YEARS



steady fall until January 1933. In 1933 the curve falls from July to a second minimum in August and then rises to a maximum in November. The divergence from July to October is the most striking difference between the two curves.

The most obvious comparison is between rate of cure and rainfall. Rainfall figures for the two years (as recorded on the estate) are plotted in Figure 5 and it is immediately noticed that the rainfall in the second half of 1933 does not rise to the same level as in the corresponding period of 1932. It is possible, therefore, that the failure of the tensile modulus to rise continually from May onwards in 1933 is associated with the comparatively low rainfall figures for the period August to November. The correlation is far from perfect and it will be noticed that the maximum modulus figure in September 1932 corresponds to a rather low rainfall figure, although it follows the extremely high rainfall of August. However, in general, it may be said that from July until January the tensile modulus shows some direct relation to rainfall.

It has already been observed that Behre (15) found a higher rate of cure (i.e. a higher modulus) in the wet season of the year. The position in the early months of the year is very different and the marked minimum in May corresponds, in 1932, to a fairly low rainfall and, in 1933, to the highest rainfall of the year. Again, the low rainfall figures in June and July correspond in each year to a rising tensile modulus. It is possible that the factors influencing rate of cure in the first half of the year are different from those operating in the second half of the year and the changing physiological activities of the tree may be of importance. It is suggested that the low rate of cure in May is caused by a shortage in natural accelerators which arises, in its turn, from the great drain on the tree represented by the development of new leaves during March and April. This would lead to the generalisation that rate of cure is approximately proportional to rainfall except during the period following wintering, when there is an exceptional fall in rate of cure independent of climatic conditions. This generalisation is in accord with the limited experimental data available and does not conflict with accepted theories of vulcanisation or of the physiology of the tree. On the other hand it does not follow as a necessary consequence of earlier knowledge or of the present experiments; there is no proof of it and it is advanced with the greatest diffidence.

Whitby's general rule connecting rate of cure with the composition of the latex is of great interest and it is possible to test this rule for the second year of the period under review. The rule, as formulated by Whitby, is as follows:—"Hence, it

"appears that it may be stated generally that an increase in the "ratio (serum substances/rubber) leads to a higher and a decrease "to a lower rate of cure. The conclusion, it may be noted, is "in accord with that which an examination of the factors in "variation involved in the preparation procedure would suggest, "viz. that increase in the amount of serum substances associated "with the rubber is favourable to rapidity of cure."

From February 1933 to January 1934 monthly samples of the latex from the four Pilmoor clones were also studied in this laboratory. The results have been published in a Bulletin by the present author (28). The examination of these samples included determinations of dry rubber content and of non-coagulable solids (serum solids) and it is possible to compare the ratio of these two determinations with the tensile modulus of the corresponding rubber samples. For simplicity only the mean values for the four clones are considered and the figures are given in Table VIII.

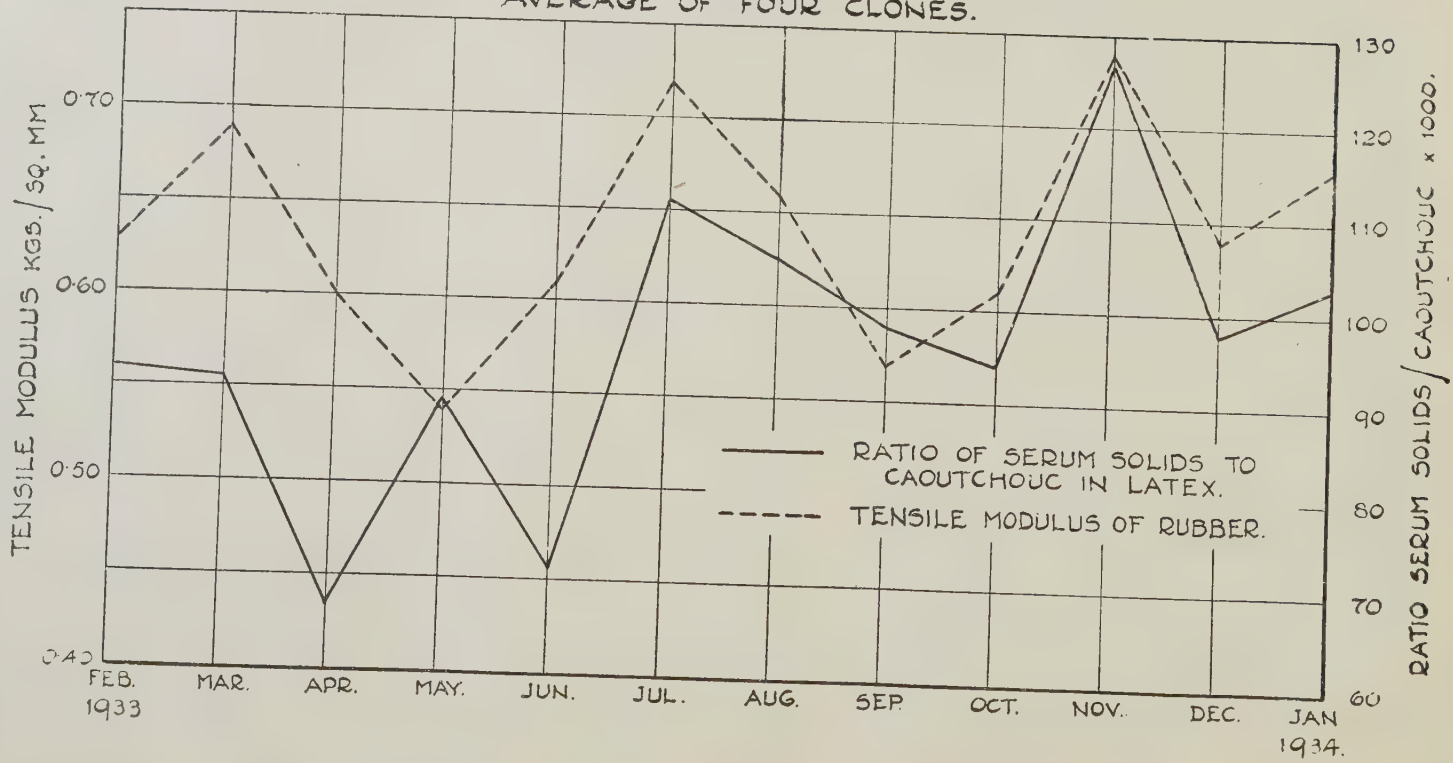
TABLE VIII

	Tensile Modulus kg./sq. mm.	Ratio Serum Solids/ D.R.C. × 1000
1933 February ...	0.63	92
March ...	0.69	91
April ...	0.60	67
May ...	0.54	89
June ...	0.61	71
July ...	0.72	111
August ...	0.66	105
September ...	0.57	98
October ...	0.61	94
November ...	0.74	127
December ...	0.64	98
1934 January ...	0.68	103

These data are plotted in Figure 6 and it will be seen that the position is somewhat similar to that in comparing tensile modulus with rainfall. From July to the end of the year there is close agreement between the two curves but the May minimum in tensile modulus is not associated with a minimum value for the ratio. It appears that in May there is a shortage of the specific accelerators which is not reflected in the percentage of total serum solids. A reasonable generalisation can again be made to the effect that Whitby's rule, as applied to seasonal variation, is a fairly satisfactory guide, except in the few months immediately after wintering.

FIGURE 6. COMPARISON OF TENSILE MODULUS WITH THE RATIO OF SERUM SOLIDS TO CAOUTCHOUC

AVERAGE OF FOUR CLONES.



Variations in Vulcanising Properties of the Seedling Rubber

The figures obtained from the area of seedling rubber adjacent to the experimental clone block are not included in the foregoing comparisons for two reasons: (a) figures are available for a portion only of the period which the experiment covers, (b) comparison is complicated by a change-over in the seedling block in January of each year. The tensile modulus figures for the period September 1932 to January 1933 are shown in Table IX:

TABLE IX

Month	Tensile Modulus kg./sq.mm.	Month	Tensile Modulus kg./sq. mm.
1932 September ...	0.69	1933 June ...	0.72
October ...	0.83	July ...	0.72
November ...	0.75	August ...	0.58
December ...	0.62	September ...	0.50
1933 January ...	0.37	October ...	0.63
February ...	0.83	November ...	0.82
March ...	0.63	December ...	0.66
April ...	0.49	1934 January ...	0.30
May ...	0.55	Mean ...	0.63
		Standard Deviation ...	0.15
		Co-efficient of variation	24 per cent.
		Mean, excluding two January figures ...	0.67
		Standard Deviation excluding two January figures ...	0.11
		Co-efficient of variation	16 per cent.

The abnormally low values for January of each year are attributable to a change in tapping panel. The fall in tensile modulus in January 1934 was accompanied by a rise in the D.R.C. of the latex from 32 to 44 per cent. (see Wiltshire, 28) and is thus a normal example of Whitby's rule and is in accord with many experiments of de Vries. Apart from this exception the figures are similar to those obtained for the four clones. The mean value is of the same order and, if January figures are excluded, there is a similar degree of variation. In 1933 the seedling rubber shows low values in April and May followed by a rise until July, a fall until August and a rise to a maximum in November. It thus follows very closely the trend of the budgrafted rubber.

Summary

(1) Among the four clones studied for a period of two years there are small but characteristic differences in rate of cure and two of the clones give rubber which is significantly faster curing than that from the other two clones. The differences observed are only very small but the principle of characteristic differences has been established and there is the possibility that clones yet unexamined may be found to give rubber of distinctly abnormal vulcanising properties.

(2) The variation between the four clones in any month is smaller than the variation in any clone over the period. The widest range in time of cure in one month is about 17 minutes (October 1932) while the least variable clone shows a range of 25 minutes over the period and the most variable a range of 35 minutes.

(3) The four clones show very similar variations in rate of cure and there is a high positive correlation between the figures for all the clones taken in pairs.

(4) These common variations can be *described* thus: the rate of cure as expressed by tensile modulus follows approximately the rainfall but there is a period of low values after the wintering season which bears no relation to the rainfall. It is possible that this description indicates the cause of the variations but there is no confirmatory evidence.

(5) During the second year the rate of cure corresponds approximately to the ratio of serum solids to rubber in the latex but, as with rainfall, the period following the wintering season is anomalous.

(6) An adjacent area of seedling rubber shows similar variations in rate of cure.

(7) Differences in tapping-height up to 40 inches do not give rise to any characteristic differences in rate of cure.

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RUBBER FROM LATEX COAGULATED WITH SULPHURIC ACID

BY

G. Martin and W. S. Davey

An article by Wiltshire in the Journal of the Rubber Research Institute, November 1932, p.94, on the use of sulphuric acid as a coagulant of latex has attracted considerable attention amongst rubber manufacturers who have expressed some alarm at the possibility of the extended use of this chemical for coagulation. The India Rubber Manufacturers' Association, Great Britain, stated "it was felt that it is highly undesirable that such a practice should be adopted without first ascertaining that recognised standards of performance, including ageing, will be maintained in the finished manufactured articles".

In view of the apprehensions of manufacturers, samples were supplied by the Rubber Research Institute to the London Advisory Committee in order to investigate as fully as possible the effect on the properties of the rubber of using sulphuric acid as a coagulant.

The samples comprised (a) two samples of smoked sheet coagulated with sulphuric acid and formic acid, prepared on a Malayan estate which regularly uses sulphuric acid as a coagulant; and (b) four samples of air-dried sheet prepared by the staff of the Rubber Research Institute. The air-dried sheet samples were in two pairs and were prepared on different days using acetic acid sheet as a control in each case. The sulphuric acid sample in the first pair was prepared using more acid than is usual on estates. Subsequently a further sample of air-dried sheet coagulated with sulphuric acid and prepared on the above Malayan estate was received for comparison with the smoked sheet samples from the same estate.

Particulars of the preparation of these samples are shown in Table I.

All the air-dried sheet samples showed signs of mould, particularly C, E and F.

The samples were divided into two portions, one of which was submitted to tests by the India Rubber Manufacturers'

TABLE I

Sample	Where prepared	Type of sheet	Coagulant.	Amount of Coagulant	D.R.C. of Latex lb./gall.	Other Details
A	A Malayan estate	Smoked	Formic acid	1 fluid oz. to 14.7 lbs. of rubber	1⅓	9 days smoking
B	A Malayan estate	Smoked	Sulphuric acid	1 fluid oz. to 25 lbs. of rubber	1⅓	9 days smoking
C	R.R.I.	Air-dried	Acetic acid	2.8 grams per lb. of rubber	1½	Soaked in water 1 hour after machining. Dried 2½ days at 110—120°F.
D	R.R.I.	Air-dried	Sulphuric acid	3.0 grams per lb. of rubber	1½	do.
E	R.R.I.	Air-dried	Acetic acid	2.8 grams per lb. of rubber	1½	do.
F	R.R.I.	Air-dried	Sulphuric acid	2.3 grams per lb. of rubber	1½	do.
G	The same estate as samples A and B.	Air-dried	Sulphuric acid	1 fluid oz. to 25 lbs. of rubber		

Association and the other to the following tests by the staff of the London Advisory Committee:—

Chemical Analysis	Determination of water soluble sulphate present
Plasticity	Hardness (D_{30}) and mastication
Rubber-sulphur mixing (a)	Vulcanisation in 100:10 rubber-sulphur mixing
(b)	Ageing in 90 : 10 rubber-sulphur mixing

Accelerator mixing (a) Vulcanisation and ageing in "Captax" mixing
(b) Vulcanisation and ageing in "D.P.G." mixing

The purpose of the chemical test is to indicate whether appreciable amounts of free sulphuric acid remain in the rubber after the coagulum has been machined with the consequent removal of a considerable proportion of the non-rubber serum substances and probably also of the sulphuric acid coagulant.

The purpose of the plasticity tests is to indicate whether the use of sulphuric acid affects the manipulation of the rubber by manufacturers.

Vulcanisation and ageing tests were carried out in three mixings. The rubber-sulphur mixing was selected as one because it gives results which are very sensitive to abnormality in the non-rubber accessory substances and to deterioration of the caoutchouc. The two accelerator mixings selected are more in accord with manufacturing conditions than the rubber-sulphur mixing. Both accelerators are popular, one representing an acidic and the other a basic type of accelerator. They may therefore react differently to traces of sulphuric acid in the rubber. They also differ in that one has antioxidant properties and the other is without effect in this direction. The proportions of the different ingredients in each mixing were selected so as not to hide variability in different samples of rubber and are also in accord with manufacturing practice.

The investigation is considered to be fairly comprehensive from a laboratory point of view, although it does not cover all the points on which manufacturers would possibly like some assurance before approving the extended use of correct proportions of sulphuric acid as a latex coagulant. It is a reasonable presumption however that, if the rubber satisfies all these tests, there is only a remote chance that it will cause difficulty in the rubber factory or shorten the life of the finished article.

Chemical Examination

Each sample was extracted (Soxhlet extractor) with boiling water for two days and the extract examined for acidity and soluble sulphate in the usual manner, with the result shown in Table II:

The acidity of the aqueous extract of the estate samples is much higher than that of the samples prepared by the Rubber Research Institute. The latter were soaked in water after machining the coagulum to sheet and it is possible that the estate

TABLE II

Sample	Coagulant	Acidity in terms of mg. of KOH per 100 gm. Rubber	Soluble sulphate (SO_4) per cent.
A	Formic Acid	13.6	0.007
B	Sulphuric „	22.4	0.020
C	Acetic „	4.8	nil
D	Sulphuric „	5.6	trace
E	Acetic „	6.4	nil
F	Sulphuric „	trace	nil

samples did not receive this treatment, which would undoubtedly remove some of the water-soluble material remaining in the rubber.

The amount of free sulphuric acid in the samples prepared by the Rubber Research Institute was so small that it could hardly be detected. There was more soluble sulphate in the estate sample coagulated with formic acid and still more in that coagulated with sulphuric acid. The maximum amount of soluble sulphate in any of the samples was 0.02 per cent, which is no more than might be incorporated with rubber by manufacturers due to the use of slightly acid sulphur or zinc oxide.

These results indicate that the amount of free sulphuric acid remaining in the dry rubber after coagulation with sulphuric acid is not sufficiently large to alarm manufacturers, particularly if the coagulum is soaked in water after machining. It is possible to use excess of sulphuric acid for coagulation and only a trace may be apparent in the dry rubber after machining and soaking the coagulum.

Plasticity

The results of plasticity tests are given in Table III.

TABLE III

Sample	Coagulant	D_{30} (mm.)	Mastication No.
A	Formic	1.56	104
B	Sulphuric	1.49	108
C	Acetic	1.51	110
D	Sulphuric	1.42	97
E	Acetic	1.51	113
F	Sulphuric	1.42	100

The samples prepared with sulphuric acid are, in general, slightly softer than the control samples and masticate on the whole more easily. It appears likely therefore that the use of sulphuric acid will have an advantageous effect as regards the manipulation of rubber by manufacturers.

Vulcanisation and Ageing

The results of vulcanisation and ageing tests are shown in the Tables IV to VIII.

Table IV Series of cures in rubber-sulphur mixing 100 : 10.

Table V Ageing tests in vulcanised rubber-sulphur mixing 90 : 10.

Table VI Range of cures in a Captax mixing.

Table VII Ageing tests in a Captax mixing.

Table VIII Ageing tests in a D.P.G. mixing.

There is no evidence that the sulphuric acid samples are weaker than the controls on vulcanisation in the rubber-sulphur or accelerator mixings. In all the mixings the sulphuric acid samples on ageing retain their strength for approximately the same period as controls. In some cases the controls are a little better than the sulphuric acid samples and in others the latter have the advantage.

TABLE IV

Mixing : Rubber ... 100
Sulphur ... 10

Sample	Tensile Strength (lb./sq. in.) after Vulcanisation at 148°C for			Elongation per cent at Load of 1.04 kg./sq.mm. after Vulcanisation at 148°C for			Calculated correct Time of Cure, i.e. to give Elong = 800.
	120 min	140 min.	160 min.	120 min	140 min.	160 min.	
							(min.)
A Smoked sheet Formic acid	1960	2130	—	883	797	—	139
B Smoked sheet Sulphuric acid	1850	2250	—	889	789	—	138
C Air-dried sheet Acetic acid	1910	2330	—	870	794	—	138
D Air-dried sheet Sulphuric acid	1180	2140	2340	930	853	800	160
E Air-dried sheet Acetic acid	1740	1950	—	893	810	—	142
F Air-dried sheet Sulphuric acid	1230	1710	2350	915	843	792	158
G Air-dried sheet Sulphuric acid	2400	2500	—	840	766	—	131

TABLE V

Mixing : Rubber ... 90
Sulphur ... 10

Sample	Time of Vulcanisation at 148°C. (min.)	Tensile Strength (lb./sq.in.) after Ageing at 70°C for Hours							Elongation (per cent) at Load of 1.04 kg./sq.mm. after Ageing at 70°C for Hours						
		0	48	96	120	144	168	192	0	48	96	120	144	168	192
A Smoked sheet Formic acid	106	1890	2520	2250	2100	1730	1930	1650	857	774	738	722	706	695	677
B Smoked sheet Sulphuric acid	106	1880	2560	2020	2160	1850	1600	1280	864	782	748	720	708	692	—
C Air-dried sheet Acetic acid	107	1830	2130	1740	1490	360	—	—	874	780	729	710	—	—	—
D Air-dried sheet Sulphuric acid	125	1990	2210	1920	1860	1550	—	—	888	796	748	724	725	—	—
E Air-dried sheet Acetic acid	115	2030	2530	2100	2070	460	—	—	853	762	706	692	—	—	—
F Air-dried sheet Sulphuric acid	125	1900	2130	1830	1460	250	—	—	875	783	731	712	—	—	—

TABLE VI

Mixing : *Rubber* ... *100*
Zinc oxide ... *6*
Sulphur ... *3.5*
Stearic acid ... *1*
Captax ... *0.5*

Sample	Tensile Strength after Vulcanisation at 126°C for 20 min.	40 min.	60 min.	80 min.	100 min. (lb./sq.in.)	Elongation at Load of 1.04 kg./sq.mm. after Vulcanisation at 126°C for 20 min.	40 min.	60 min.	80 min.	100 min.
A Formic acid Smoked sheet	1180	1830	2320	2410	2280	—	849	775	741	744
B Sulphuric acid Smoked sheet	1000	2030	2030	2540	2360	—	849	788	743	746
C Acetic acid Air-dried sheet	1120	1590	2050	2280	2310	—	884	808	784	783
D Sulphuric acid Air-dried sheet	1280	2090	2430	2570	2390	—	843	794	767	761
E Acetic acid Air-dried sheet	730	1770	2080	2080	2160	—	890	867	807	810
F Sulphuric acid Air-dried sheet	240	1430	1920	2120	2330	—	—	905	860	847
G Sulphuric acid Air-dried sheet	1200	2210	2300	2350	2360	—	837	796	766	763

TABLE VII

Mixing : *Rubber* ... *100*
Zinc oxide ... *6*
Sulphur ... *3.5*
Stearic acid ... *1*
Captax ... *0.5*

Sample	Time of Vulcanisation at 126°C (min.)	Tensile Strength (lb./sq.in.) after Ageing at 82.5°C for Days							Elongation (per cent) at Load of 1.04 kg./sq.m.m. after Ageing at 82.5°C for Days						
		0	2	4	6	8	10	12	0	2	4	6	8	10	12
A Formic acid Smoked sheet	80	2290	2770	2480	1840	500*	960	230	736	629	616	575	—	—	—
B Sulphuric acid Smoked sheet	80	2650	2330	2770	2330	1990	1560	740	734	664	642	613	574	560	—
C Acetic acid Air-dried sheet	80	2430	2770	2340	2150	1630	1520	750	771	663	651	623	587	563	—
D Sulphuric acid Air-dried sheet	80	2320	2550	2030	2340	850	890	200	721	660	653	619	—	—	—
E Acetic acid Air-dried sheet	80	2120	2570	2430	1980	1810	1370	710	775	690	681	644	626	603	—
F Sulphuric acid Air-dried sheet	100	2220	2140	2100	1690	1190	710	190	776	725	719	683	—	—	—
G Sulphuric acid Air-dried sheet	80	2650	2500	2200	1560	390	235	250	731	644	633	596	—	—	—

*Probably two exceptionally weak rings

TABLE VIII

Mixing : *Rubber* ... *100*
Zinc oxide ... *6*
Sulphur ... *2.75*
D.P.G. ... *0.4*

Sample	Time of Cure. at 141°C. (min.)	Tensile Strength (lb./sq.in.) after Ageing at 82.5°C for Days						Elongation (per cent) at Load of 1.04 kg./sq.mm. after Ageing at 82.5°C for Days					
		0	2	4	5	6	7	0	2	4	5	6	7
A Formic acid Smoked sheet	60	2050	2500	1500	1060	510	260	787	744	777	—	—	—
B Sulphuric acid Smoked sheet	60	2580	2400	1550	1450	1000	200	752	718	740	740	—	—
C Acetic acid Air-dried sheet	60	2450	1640	1200	1110	250	170	735	694	730	—	—	—
D Sulphuric acid Air-dried sheet	60	2160	2270	1460	1400	915	430	770	735	764	774	—	—
E Acetic acid Air-dried sheet	60	1980	2120	1250	1180	740	340	774	723	753	—	—	—
F Sulphuric acid Air-dried sheet	60	2370	2200	1160	660	160	170	795	762	780	—	—	—

The sulphuric acid coagulated air-dried sheets prepared at the Rubber Research Institute required approximately 14 per cent. longer vulcanisation than the controls in rubber-sulphur mixings, but the rate of vulcanisation of the smoked sheet and air-dried sheet prepared on a Malayan estate is hardly affected by the use of sulphuric acid. The latter results are contrary to general experience, and in a number of cases it has been observed that the estate samples differ in their relative behaviour from those prepared at the Rubber Research Institute. It is possible that the estate samples are abnormal and that definite conclusions should be confined to those drawn from the results given by the Rubber Research Institute samples.

In the Captax mixing there is little difference between the estate samples, but the two pairs of air-dried sheets from the Rubber Research Institute show small differences which are in opposite directions.

In the D.P.G. mixing the air-dried sulphuric acid sheets prepared at the Rubber Research Institute give a softer vulcanisate than the controls, but the estate smoked sheet displays the opposite effect.

In the Captax mixing the sulphuric acid samples display a smaller increase in modulus during ageing than the other samples. This is an advantage but it is not important and is not displayed in the other mixings.

It appears from these results that the most important effect of the use of sulphuric acid is an alteration in rate of vulcanisation, particularly in the rubber-sulphur mixing, and it is evident that the use of sulphuric acid on some estates and of acetic and formic on other estates must tend to increase variability and thereby prejudice manufacturers against the use of first-grade rubber.

The effect of the sulphuric acid when used in correct proportion is very small, however, when compared with the total variability which already exists. The rubber from some estates using formic or acetic acid as a coagulant may vulcanise twice as fast as that from others using the same coagulant, whereas the retardation of vulcanisation owing to the use of sulphuric acid is less than 20 per cent. and may in some cases be much less.

In the case of accelerator mixings the effect of using sulphuric acid cannot be measured in terms of rate of vulcanisation owing to the slow alteration in physical properties with period of vulcanisation, but the limited data available indicate that the use of sulphuric acid would lead to an increase in variability which is small compared with that already existing in rubber from different estates.

The India Rubber Manufacturers' Association arrived at similar conclusions from the results of their tests on portions of the samples. Their report is as follows:—

"With regard to the rubber coagulated with sulphuric acid it was found that, in every case, the rubbers so coagulated were slower curing than the standard rubbers in pure rubber stocks not containing added accelerator. When adjustment was made for this slowing-up in curing the ultimate physical properties of the above were satisfactory.

When stocks were used containing accelerators different results were obtained depending on the choice of the accelerator. With an accelerator of the type of mercapto-benzothiazole increased activation was obtained in the case of rubbers coagulated with sulphuric acid whilst in the case of accelerators such as D.P.G., where best results obtained with alkaline conditions, retardation was again found.

It was again found that when these factors were recognised and the articles cured to an equivalent state of cure, similar ageing properties were obtained. It would, therefore, appear from the tests carried out that coagulation with sulphuric acid under properly controlled conditions could give rubbers with intrinsic properties equal to those obtained with standard methods of preparation. Our tests, however, do suggest that a rubber manufacturer who unwittingly received a substantial part of his deliveries in the form of rubber coagulated with sulphuric acid might encounter definite manufacturing trouble due to the rate of vulcanisation being abnormal, and due to the fact that variable results would obtain according to the type of accelerator being used and the type of article being manufactured.

We think that you will realise that owing to the small size of the samples sent, only laboratory tests could be carried out, and it was not possible to make a variety of manufactured articles which could be put to service tests. The tests, however, do serve to show that the use of sulphuric acid requires very careful consideration on the part of rubber growing interests, and they do definitely indicate the possibility of normal manufacture being thrown out of gear due to the properties of the sulphuric acid coagulated rubber being abnormal with regard to cure.

We therefore advise that rubber coagulated with sulphuric acid should not be put on the market without the method of coagulation being definitely stated."

Summary

The results of tests carried out in the laboratories of the London Advisory Committee show that when sheet rubber is prepared by coagulation of latex with sulphuric acid

(1) only a trace of free sulphuric acid remains in the dry rubber,
(2) the rubber is somewhat easier to manipulate in rubber manufacturing operations than that prepared by coagulating latex with acetic acid,
(3) the rubber has satisfactory mechanical properties when vulcanised in rubber-sulphur or accelerator mixings,
(4) the rubber ages satisfactorily in rubber-sulphur and accelerator mixings,
(5) the use of sulphuric acid would tend to increase the variability in vulcanisation of first-grade rubber unless its use became general.

Conclusions

The use of correct proportions of sulphuric acid as a coagulant is not harmful to the intrinsic properties of the rubber. On the other hand the economy due to its use is not large (.014d. per lb. rubber) and there is a possibility of harm arising in two directions, viz.

(1) As long as it is used by only a proportion of estates it will increase slightly the variability of rubber and so tend to prejudice all manufacturers against first-grade rubber in favour of lower grades in which a high degree of uniformity cannot reasonably be expected. There is no doubt that some manufacturers view with apprehension the possibility of an increase, however slight, in the variability of first-grade rubber. In addition, manufacturers of high grade special articles would be unwilling to use on a large scale rubber which they knew had been coagulated with sulphuric acid unless they first had an opportunity of making prolonged and thorough tests with their own products.

(2) The accidental use of excess of sulphuric acid, in addition to causing difficulty on an estate, is known to have a definitely harmful effect on the rubber. The use of excess of acetic or formic acid has no serious effect on the properties of the rubber.

It is not anticipated that the plantation industry would suffer serious disadvantage from the general use of sulphuric acid as a coagulant, but the economy does not appear to be sufficient to justify the risk, especially in view of the objections raised by manufacturers.

22nd February, 1934.

Discussion and Recommendations on the foregoing Paper

BY

J. L. Wiltshire and E. Rhodes

The report on the examination carried out at the laboratories of the London Advisory Committee and by the India Rubber Manufacturers' Association on rubber from latex coagulated with sulphuric acid and supplied by the Rubber Research Institute, is very opportune. It confirms many of the statements made in the paper on this subject already published in this Journal by one of us (J.L.W.) and offers an opportunity for some general remarks on the situation.

The previous paper was written in October 1932 and published in the Journal in December 1932 [*J.R.R.I.M.* 4 (1932) 94]; since then various remarks in the press and in correspondence addressed to us have shown that many commentators have formed an incorrect opinion on the views expressed in that paper. It would seem to be believed in some quarters that the Rubber Research Institute has deliberately recommended the use of sulphuric acid as a coagulant with a fine disregard, or in complete ignorance of the possible repercussions of such a recommendation. It is therefore necessary to refer to the conditions under which that paper was published and, briefly, to its subject-matter.

In October 1932 the price of rubber was 7.48 cents per lb. and at the date of publication, December 1932, it was 7.61 cents per lb. The price showed no indication of recovery and the vast majority of rubber producers were working at a loss. Work at this Institute was therefore of necessity directed to some extent into a search for methods of reducing costs and the provision of relevant information to any producers desirous of experimenting with various methods. In these circumstances the possible use of a cheaper coagulant could not be overlooked and there were many enquiries as to the desirability of using sulphuric acid which had previously been used in times of acetic acid shortage. The object of the paper was to circulate more widely the views expressed in our advisory correspondence and to adduce confirmatory experimental evidence.

The paper opens with a brief summary of published literature; it continues with a description of experiments designed to show the optimum conditions for coagulation; further experiments are then reported to prove that rubber produced under these optimum

conditions is satisfactory in relation to those tests which it was possible to carry out in this laboratory. The saving effected by the use of sulphuric acid was estimated at 0.05 cent per pound.

It was also pointed out that, in some quarters, there would be opposition to the marketing of rubber prepared by the use of sulphuric acid sheet. It was suggested that estates wishing to adopt this coagulant should first submit samples of the new product in the normal market. To stress the marketing difficulty the warning against sulphuric acid issued by the Rubber Growers' Association in 1926 was quoted in full. Against this warning two arguments were advanced (a) that a saving of 0.05 cent per pound was of infinitely greater importance in 1932 than in 1926, (b) that the use of sulphuric acid in minimum quantities would not increase very greatly the considerable degree of variability already existent in plantation sheet rubber.

The last paragraph of that paper gives the key to the position as envisaged by the Institute at that time and is quoted in full:

> "It is impossible for us definitely to recommend the use of sulphuric acid, since the varying requirements in different markets render the problem as much commercial as technical. It is possible to produce a good quality rubber by the use of sulphuric acid, provided sufficient care is exercised, but even the best rubber thus produced may prove unwelcome if it falls into the hands of a buyer who has a fundamental and longstanding objection to the coagulant."

Correspondence with kindred organisations in Ceylon, Sumatra and Java reveals the facts that in Ceylon no estates have so far used sulphuric acid and that in the Dutch East Indies only one or two estates use it. The various notes of warning, which were sounded in the previous publication from this Institute, are similarly sounded in the Dutch East Indies by the organisations concerned, and the few estates which use the acid do so not with deliberate encouragement but in the full knowledge of the difficulties and complications involved.

At the present time (April 1934) the only change in the position is the increased price of rubber, and this affects the position materially.

The present report by Messrs. Martin and Davey reveals no technical objections to the use of sulphuric acid except a slight increase in time of cure and this fact in itself would not seem to be of very vital importance. The authors in discussing the experimental results say "The effect of the sulphuric acid, when used "in correct proportion, is very small when compared with the "total variability which already exists. The rubber from some "estates using formic or acetic acid as a coagulant may vulcanise

"twice as fast as that from others using the same coagulant, "whereas the retardation of vulcanisation owing to the use of "sulphuric acid is less than 20 per cent. and may in some cases "be much less." It is, however, the opinion of the authors that "the use of sulphuric acid would tend to increase the variability "in vulcanisation of first-grade rubber unless its use became "general."

The report, as a whole, and particularly the section contributed by the India Rubber Manufacturers' Association, makes it clear that the use of sulphuric acid is not welcomed at present; the experimental results reveal no really objectionable features, but it is felt that there may nevertheless be unsuspected disadvantages in cases where a manufacturer received a supply of rubber without being aware of the fact that sulphuric acid had been used in its preparation. From the producers' viewpoint therefore the outstanding feature is that there is not a universal acceptance of sulphuric acid coagulated rubber and as in 1932 so in 1934, it is "impossible for us definitely to recommend the "use of sulphuric acid since the varying requirements in different "markets render the problem as much commercial as technical."

It is believed that none of the comparatively few estates, which adopted the use of sulphuric acid as an emergency measure, did actually take the advice of the Institute and submit samples of the product in the normal market; rather did they market the rubber through the usual channels without indicating the nature of the coagulant used in its preparation. In this they followed the example set by a few estates on which sulphuric acid had been in common use for many years previous to the period of depression. These producers have been able to sell their product at top prices for many years, have received no complaints on the quality of the rubber and have at no time been called upon to declare the nature of the coagulant used. During the past two years the use of sulphuric acid has probably increased slightly but we have received no reports of poor quality or deterioration in storage of the rubber prepared in this manner. In view of the fact that no broker or other buyer appears to demand a certificate of preparation, estates have not generally accepted the suggestion of the Institute and have marketed the rubber without giving an indication that sulphuric acid was used in its preparation. Consignments of rubber reaching England are assumed by the manufacturer to be material prepared by the use of acetic acid or formic acid unless otherwise stated, and it is not difficult to understand the uneasiness which arises in the mind of the manufacturer at the thought of receiving unknowingly a consignment which might not in fact consist of one of those types of rubber to the

processing of which he is accustomed, and with the peculiarities of which he is by experience aware. It is perhaps regrettable that there exists no system of declaration under which producers would be called upon to certify the nature of the coagulant used in the preparation of each consignment; neither the broker nor the user, who is most nearly affected, appears to press for such a system which would at once relieve the uneasiness in the mind of the user, and in the long run the more quickly establish firmly, or on the other hand completely and finally dis-establish, any type of rubber of which users had not had experience. It should be remembered that, while the Institute can give technical advice, and while it can bring new products to the notice of some users, it is powerless to overcome a natural aversion of users as a body to the adoption of a material prepared in an unusual manner. In order to overcome such aversion the user should be given an opportunity to buy the certificated article and test for himself at leisure its suitability; thus and thus only can the article make for itself an assured market. If sulphuric acid rubber is to establish itself in face of the doubts and fears, which rightly or wrongly exist in the minds of users, it can never properly do so by a perpetuation of the present method of marketing which, if it does not encourage, certainly does nothing to deter an estate from marketing a product which the user buys assuming it to be a different product. If the product be similar in its properties to rubber prepared by the use of formic acid or acetic, this fact will in no way alter the user's fear of sulphuric acid sheet rubber for he will not be aware that he has ever had it.

In the absence of a system of declaration rubber prepared by the use of sulphuric acid has at the present date neither general acceptance nor a mass of technical testimony based on large-scale practice to condemn it.

The new technical evidence now presented, although obtained in small-scale tests, actually serves to strengthen rather than to refute the views expressed in the previous publication, that a rubber of good quality can be produced by the intelligent use of sulphuric acid.

The welcome improvement in the price of rubber has however now made it less important to seek economies of the order of 0.05 cent per pound of rubber. Because of this fact and of the uneasiness which the undeclared use of sulphuric acid may create in the minds of users, the few estates which are using sulphuric acid are advised not to continue this method of preparation without declaring the fact to the purchasers of their product.

Kuala Lumpur,
25th April, 1934.

RUBBER FROM DILUTE LATEX

BY

G. Martin, W. S. Davey, H. C. Baker and E. Rhodes

A series of samples of air-dried sheet was prepared from very dilute latex and the manipulative and water-absorption properties were examined in comparison with those of similar samples of crepe, in order to ascertain whether rubber from much-diluted latex possessed improved properties over normal estate crepe and sheet.

Plasticity

The sheet samples were submitted to the usual plasticity tests and the results given in Table I were obtained.

TABLE I

Sample	Dry Rubber Content of Latex (lb./gall.)	D_{30} (mm.)	Mastication No.
B 84/1	1½	1.50	108
B 84/2	¼	1.46	104
B 85/1	1½	1.47	114
B 85/2	¼	1.45	111

The results in Table I show that dilution of the latex has had little effect on the plasticity of these samples. They were tested soon after arrival in London and general experience with regard to the cause of variation in plasticity indicates that, if they had been kept for some time, the air-dried sheet from the very dilute latex would have become soft owing to the reduction in the amount of serum substances which protect the rubber against oxidation. The samples were therefore submitted to an accelerated ageing test by heating in air at 100°C. The results given in Table II shew the effect of this treatment.

These results in Table II shew that the two controls differ markedly in their resistance to oxidation and that the dilution of the latex with consequent removal from the rubber of part of the natural antioxidants decreases this resistance.

TABLE II

Sample	Dry Rubber Content of Latex (lb/gall.)	D_{30} Original (mm.)	D_{30} After heating for 17 hours at 100°C. (mm.)
B 84/1	1½	1.50	0.78
B 84/2	¼	1.46	0.47
B 85/1	1½	1.47	1.39
B 85/2	¼	1.45	0.51

This was confirmed by the examination of the crepe samples. The results of heating at 100°C for 4 and 17 hours respectively are given in Table III.

TABLE III

Sample	Dry Rubber Content of Latex (lb./gall.)	D_{30} Original (mm.)	D_{30} After heating for 4 hours at 100°C (mm.)	D_{30} After heating for 17 hours at 100°C (mm.)
A	1½	1.37	0.54	Too soft to test, practically liquid
B	½	1.28	0.39	do
A_1	½	1.25	0 52	do
B_1	(6 oz.)	1.18	0.49	do
C_1	¼	1.13	0.49	do
A_2	1½	1.28	1.08	0.81
B_2	¼	1.19	0.90	Too soft to test

As in the case of the previous series the control samples (normal dilution) differ somewhat in their resistance to oxidation, and the dilution of the latex definitely decreases this resistance. It is probable that rubber from dilute latex would become soft more quickly on keeping than rubber from latex of normal dilution, but there is no evidence that rubber from dilute latex cannot be stored for quite long periods without serious deterioration.

Moisture Absorption

Rubber from dilute latex probably contains less serum substances than rubber from latex of normal dilution and should

therefore have a reduced tendency to absorb moisture from a damp atmosphere. As there is a demand from the electrical industries for rubber of this type the samples were submitted to moisture-absorption tests by leaving thin pieces of each sample suspended over a saturated solution of potassium chloride for eight days at 15°C (84.6 per cent relative humidity). The results are shewn in Table IV.

TABLE IV

	Sample	Dry Rubber Content of Latex (lb./gall.)	Amount of Moisture absorbed (per cent.)
Series I	B 84/1	1½	0 92
	B 84/2	¼	0.85
	B 85/1	1½	0.82
	B 85/2	¼	0.71
Series II	A	1½	0.65
	B	½	0.50
	A_1	½	0.51
	B_1	6 oz.	0.46
	C_1	¼	0.50
	A_2	1½	0.65
	B_2	¼	0.51

In each case the samples from very dilute latex absorb less moisture than those from latex coagulated at the normal dilution, but the difference is much less than that which occurs between "standard" rubber from different estates. It is unlikely therefore that the effect of dilution is sufficiently marked to be of practical importance.

Summary

Rubber from dilute latex is not more plastic or more easily manipulated than normal estate rubber when tested soon after arrival in London, but artificial ageing tests indicate that dilute latex rubber would probably become softer on keeping for a long period than rubber from latex of normal dilution.

Rubber from dilute latex absorbs slightly less moisture than rubber from normal latex but the difference is not sufficiently marked to be of importance to the electrical industries.

As far as these investigations are concerned rubber from dilute latex offers no important advantages over ordinary estate crepe and sheet.

Kuala Lumpur
3rd March. 1934

RUBBER FROM AUTOCLAVED LATEX

BY

G. Martin and Edgar Rhodes

There is a demand in the rubber manufacturing industry for rubber which is very plastic and easily manipulated. A softened rubber prepared from crepe and sheet is now being sold at a premium, but its preparation requires special plant and is protected by patent.

A number of alternative methods of preparing very soft rubber have been investigated by this Institute. One is a method suggested by Mr. D. Graham of Teluk Anson, Perak, and consists of the coagulation of latex by heating in an autoclave. Mr. Graham supplied three samples of crepe rubber prepared by this process.

The latex in the autoclave was raised to a temperature of 145°C over a period of 30 minutes, kept at that temperature for 60 minutes, and then slowly cooled. The heat treatment caused the latex to coagulate without the addition of a coagulant and the coagulum so obtained was machined into thin crepe in the usual way. The same procedure was employed in the preparation of all the samples, but they were prepared at different times, and the last two were obviously soft and were therefore submitted for examination in the laboratories of the London Advisory Committee with a view to determining their suitability for manufacturing purposes, particularly as regards ease of manipulation.

Two further samples were prepared by this Institute and for this purpose three gallons of fresh latex in an open pail were placed in an autoclave and the pressure was slowly raised to give a temperature of 149°C; this occupied 25 minutes. The full pressure was maintained for 60 minutes more and the autoclave was then allowed to cool overnight. The next morning the contents were examined; coagulation had taken place at the exposed surface and down the sides after the manner of the crust on a loaf of bread. This crust was removed, machined into crepe, and forms sample B 80/1. There remained a very thick curd-like mass which was returned to the autoclave and treated exactly as before; coagulation took place but the serum still contained a good deal of rubber. This second coagulum was machined into crepe and forms sample B 80/2. These samples were also forwarded to the London Advisory Committee for examination.

The samples were small and it was not possible to make a thorough examination in London, but sufficient quantitative data were obtained to indicate the main characteristics of the rubber.

Plasticity

The results of plasticity tests are given in Table I:

TABLE I

Sample	Prepared by	D_{30} (mm.)	Mastication No.	Relative Viscosity of 1 per cent solution of unmasticated Rubber (Benzene = 1)
A	Graham	1.16	74	...
B	„	1.09	68	...
C	„	1.00	61	...
B 80/1	R. R. I.	1.29	74	32
B 80/2	„	1.30	70	27

The D_{30} tests shew that the samples prepared by Mr. Graham are extremely soft. The average hardness of Ceylon crepe is 1.7 mm. and the range is from 1.35 to 2.00 mm. The samples are therefore much softer than any estate samples. They are not as soft however as the "softened" rubber now on the market.

Considering the softness of Mr. Graham's samples they are surprisingly difficult to masticate. It is necessary to pass them between the mixing rolls about 68 times to reach the arbitrary standard of plasticity adopted for testing purposes. Estate crepe and sheet from Ceylon require from 69 to 130 passes between the rolls to reach this degree of plasticity. Mr. Graham's samples are therefore only slightly more easily masticated than some samples of estate crepe and sheet and they compare very unfavourably with the softened rubber now on the market which requires no mastication. It is possible that steam has changed the accessory substances in the rubber so that the rubber is more resistant to the softening action of oxygen during mastication.

The two samples prepared by the Institute are somewhat harder than those prepared by Mr. Graham and, although one of them received two periods of heating, it does not appear to be softer than the other.

The viscosities of the solutions of the samples prepared by the Rubber Research Institute are about half those of standard crepe. The reduction in viscosity is not sufficiently marked to be of interest to manufacturers.

Vulcanisation

The results of vulcanisation tests in a rubber-sulphur mixing (100 : 10) at 148°C are given in Table II.

TABLE II

Vulcanisation (min.)	A		B		C	
	Tensile Strength (lb./sq. in)	$E_{1\cdot00}$* (per cent)	Tensile Strength (lb./sq.in)	$E_{1\cdot00}$* (per cent)	Tensile Strength (lb./sq. in)	$E_{1\cdot00}$* (per cent)
60	—	—	1450	960	—	—
70	1400	933	1850	885	—	—
80	1900	870	1950	793	—	—
100	2140	799	1200	710	1810	913
120	1830	724	—	—	1920	824
140	1120	660	—	—	420	—

*$E_{1\cdot00}$ = Elongation at load of 1.00 Kg./sq.mm.

These results shew that the samples display considerable variation in rate of vulcanisation. It is calculated that sample B vulcanises in 79 min., sample A in 100 min. and sample C in 125 min. The average for Ceylon blanket crepe is 138 min. and the range is from 95 to 159 min. All the samples therefore vulcanise more quickly than average Ceylon crepe. The strength of the samples is almost as good as estate crepe and sheet which usually has a maximum tensile strength between 2000 and 2400 lb./sq.in. "Softened" rubber prepared by oxidation gives poor strength results (about 1500 lb./sq.in.) when tested in this mixing, although the strengths are satisfactory in other mixings.

Chemical Examination

It has been found in previous experiments that, when creped coagulum is immersed in hot water, there is a marked reduction in the "acid value" of the dry rubber. These samples were therefore submitted to chemical examination to determine the effect of autoclaving the latex in the absence of a coagulant. The results shown in Table III were obtained.

TABLE III

Sample	Acetone Extract (per cent.)	Acid value (mgm. KOH per 100 grm. rubber)
A	2.98	91.2
B	2.94	69.5
C	3.28	86.6

The amounts of the acetone extracts are normal, but the acid value of the extracts are only one quarter to one third of the usual value for crepe and sheet.

The effect is similar to that of hot water on wet coagulum. It is strange that after the rubber has been dried, hot water no longer has this effect. In view of the low acid value of these samples it would be necessary to add additional stearic acid to many technical mixings when using rubber prepared according to this process. The need for additional stearic acid is not an important disadvantage but difficulties might occur if manufacturers were unaware of the low acid value of this type of rubber.

Summary

Crepe rubber from autoclaved latex is definitely softer, more easily masticated and gives solutions of lower viscosity than estate crepe or sheet but does not offer the manufacturers the manipulative advantages of softened rubber now on the market.

When vulcanised in a rubber-sulphur mixing it is much stronger than would be expected for soft rubber. It would be necessary to use an increased proportion of stearic acid in many technical mixings when using this rubber.

The samples supplied display considerable variation in rate of vulcanisation in a rubber-sulphur mixing, but it is necessary to obtain extensive experience with a large range of samples before conclusions can be drawn as to the extent of variability.

Conclusions

Although the samples prepared by Mr. Graham and by the Institute are soft, their manipulative advantages are not sufficiently marked to ensure a premium.

This method of preparation involves a certain amount of expense and is not free from difficulty, so that a premium is

essential if this method is to be adopted on estates. The samples have not been tested exhaustively but it is unlikely that more detailed tests would yield results which would render it necessary to modify this opinion.

Kuala Lumpur,
5th April, 1934.

NOTE ON THE INCORPORATION OF A RUBBER SOFTENER WITH LATEX AND ITS EFFECT ON THE PLASTICITY OF THE RUBBER

BY

G. Martin, W. S. Davey, H. C. Baker and E. Rhodes

There is a demand for soft, plastic rubber which offers the advantages of being easily mixed with large quantities of compounding ingredients and easily moulded to the shape required. An extremely soft rubber not only reduces the consumer's cost of manipulation but also extends the field of application of rubber. The manufacturer, when working with ordinary grades of rubber, frequently adds softeners to improve processing but these are not altogether satisfactory. A new proprietary softener named "Plastogen" for which many advantages are claimed has recently been placed on the market. It was considered likely that, if a small quantity of this softener could be incorporated with latex before coagulation, the resultant rubber would be much more easily manipulated than usual and would therefore be more acceptable to the manufacturer on this account.

Many of the proprietary softeners available are unsuitable for incorporation with latex, since they are resinous, insoluble in water and extremely difficult to emulsify; it is essential that the softener be capable of ready and homogeneous dispersion with latex so as to produce a uniform rubber on coagulation. Plastogen is a mobile liquid which, while not freely miscible with water, can, it was found, be dispersed to form an aqueous emulsion which is readily miscible with latex from which a smooth and uniform coagulum can be obtained. This softener was therefore chosen for experiment and a number of air-dried sheet samples obtained from latex-Plastogen mixtures were subjected to plasticity tests in comparison with air-dried sheet from the same crop of latex to which no Plastogen had been added.

Experimental

A 20 per cent emulsion of Plastogen in water was prepared at the Rubber Research Institute by passing the mixture thirty times through a Premier Paste Mill with a clearance of 3/1000 inch. The emulsion was added to a latex containing 1½

lbs dry rubber per gallon in proportions chosen so as to give approximately 1, 2, 3 and 5 per cent by weight of Plastogen calculated on the weight of dry rubber present. Coagulation was then carried out, using 3 fluid ounces of 5 per cent. acetic acid per gallon of latex. In all cases coagulation was good and the resulting serum was clear. The coagula were machined into sheet, allowed to drain for two hours and dried in hot air at 120°F for 46 hours. The dry sheets showed no signs of softness or stickiness when despatched from Malaya to the laboratories of the London Advisory Committee for plasticity tests. The results of these tests are given in Table I.

TABLE I

Group	Plastogen emulsion added (ccs. per gal. of 1½ lb. latex)	Weight of Plastogen calculated on rubber (per cent.)	D30 mm.	Mastication No.
A	Nil	Nil	1.44	93
B	40	0.97	1.44	89
C	80	1.94	1.34	91
D	120	2.91	1.40	79
E	200	4.85	1.35	75

In a further experiment samples of rubber were prepared in a similar manner but containing approximately 20 per cent of Plastogen, calculated on the dry rubber. The results of hardness and mastication tests are given in Table II.

TABLE II

Sample No.	Plastogen on dry rubber Per cent.	D30 (mm.)	Mastication No.
B 91/1	Nil (control)	1.52	105
B 91/2	About 20	1.01	53

The rubber containing 20 per cent. Plastogen was much softer than the samples containing smaller amounts, but it was not sufficiently soft to render mastication unnecessary, as in the case of "softened rubber" marketed by a firm in Great Britain. The rubber containing 20 per cent Plastogen was also submitted along with its control to a "Recovery" test, which is a measure of elasticity. This property is of considerable practical importance in

manufacturing operations such as calendering, extruding, etc. After squeezing or pressing to shape through rolls or dies, rubber always recovers its shape to a certain extent so that material shaped to accurate dimensions is difficult to obtain and there is frequently formed a considerable amount of scrap which is usually worked up with new material and then re-shaped. A soft rubber should have little elasticity in order to increase its advantage to manufacturers. The results obtained after passing the Plastogen sample through masticating rolls 50 times and the control sample 100 times are given in Table III. By this treatment the samples were masticated so as to reach a degree of plasticity suitable for manufacturing practice.

TABLE III

Sample No.	No. of grindings	Plasticity K	Compression at 100°C (per cent.)	Recovery Per cent of compression 1 min.	5 min.	24 hours.
B 91/1	100	0.29	54	25.5	53.1	62.4
B 91/2	50	0.29	54	38.6	62.0	78.3

These results shew that, although the Plastogen and control samples have been masticated to give the same plasticity figures, it would be necessary to masticate the Plastogen sample still further to reduce its elasticity to that of the masticated control.

Discussion

The tests for hardness and plasticity indicate that, in so far as concerns manipulative properties, rubber prepared from latex treated to give up to 5 per cent of Plastogen in the dry rubber possesses little advantage over a rubber from untreated latex. The advantage becomes somewhat more marked in rubber from latex treated to give 20 per cent. of Plastogen, but it is not comparable with that obtained by an oxidative softening of rubber. There is no evidence that Plastogen decreases the elasticity of the rubber except in so far as it increases plasticity and ease of manipulation. The softening effect produced by Plastogen in amounts up to 5 per cent would be sufficient to obviate the production of occasional samples of hard rubber which cause some difficulty to certain manufacturers but, even when incorporated in amounts up to 20 per cent, it falls short of the true objective, which is a rubber sufficiently soft to require little or no mastica-

tion, while possessing at the same time other processing advantages.

The results described confirm those obtained in the laboratories of the London Advisory Committee in experiments with preserved latex and Plastogen, and it now seems clear that substances which give efficient softening when added to the dry rubber at the time of mastication do not necessarily produce the same degree of softening when incorporated into latex and brought down with the rubber itself during coagulation. The reason for this is obscure and no explanation can at present be attempted.

Summary

The addition of the proprietary softener Plastogen to latex before coagulation has little or no commercial prospects in that it does not yield a rubber which is sufficiently soft to warrant its acceptance as a soft rubber for which a premium might be obtained.

Kuala Lumpur,
3rd. March, 1934

RUBBER FROM LATEX-BITUMEN MIXTURES

BY

G. Martin, W. S. Davey, H. C. Baker and E. Rhodes

When reclaimed rubber is incorporated into a rubber mix it increases the degree of "deadness" of the batch so that in extrusion and similar processes the rubber retains more accurately the shape given to it by the extrusion die. The "deadness" of reclaim is therefore a desirable property and it was sought to discover whether rubber-bitumen mixtures prepared on the plantations would also have the property of "deadness" and be able to substitute for reclaim in some of its applications.

Rubber-bitumen sheets were prepared from mixtures, in various proportions, of latex and the bituminous emulsion marketed under the trade name of "Colas." Coagulation was carried out with acetic acid and was somewhat uneven, with the result that samples containing a high proportion of bitumen tended to "bleed" bitumen at isolated points on their surfaces during the process of drying in hot air. This defect was however overlooked and the dry samples containing up to 40 per cent. bitumen (see Table I) were submitted to tests by the staff of the London Advisory Committee and portions were also submitted to the chief chemists of two large rubber manufacturing firms in Great Britain who reported as follows :—

(1) "Increasing amounts of bitumen definitely increase the plastic flow and decrease the recovery from pressure as measured by the Williams plasticity recovery method ..... The amount of bitumen used in these samples is considerably more than is normally used in the manufacture of high-quality rubber articles. Our tests have shewn the quality of the rubber-bitumen mixture to be more inferior as the bitumen was increased. Thus the bitumen would have to be considered as an adulterant or a cheapener as well as a softener. If required, the bitumen could undoubtedly be mixed with rubber at the manufacturing plant more economically than at the plantation because of savings in transportation costs on a basically cheap material."

(2) "No appreciable advantage over similar mixtures prepared by the ordinary method of mixing. It must be

TABLE I

Extrusion

Sample	Description of Sample	Acetone extract 24 hours extracted (per cent.)	Specific Gravity	Hardness D30 (mm.)	Mastication No.	No. of Grindings	K	Rate of Extrusion at 1450 lb./sq.in. (cc./hour)
A	Control air-dried sheet	2.75	0.906	1.64	94	90	0.23	77
B	Rubber 90 Bitumen 10	8.95	0.917	1.41	69	70	0.34	89
C	„ 80 „ 20	17.16	0.929	1.20	45	70	0.83	120
D	„ 70 „ 30	23.74	0.940	1.07	About 20	50	0.95	175
E	„ 60 „ 40	34.28	0.956	0.78	Probably nil	50	3.30	400

remembered also that if rubber is desired in a softened condition more effective softeners are available which could be used in smaller proportions. I fear that the compositions as submitted have little advantage or prospects."

The results of the plasticity tests carried out by the staff of the London Advisory Committee are shown in Table I.

The amounts of acetone-soluble material in these mixtures shew that the proportion of bitumen present corresponds approximately with that calculated at the Rubber Research Institute from the amount of bituminous emulsion added to the latex.

The bitumen has a softening effect on the rubber, but 40 per cent. of bitumen is required to give a product as soft as masticated rubber.

The mixtures were masticated and extruded through a circular orifice and the diameters of the extruded worms determined with a view to calculating "recovery" or "deadness." There was little difference in the diameters of the worms, but no conclusions as regards "deadness" could be drawn owing to marked differences in the rate of extrusion of the different samples.

Vulcanisation tests were carried out on samples B, D and E in a rubber-sulphur mixing (100 : 10) with the results shown in Table II. The samples vulcanise slowly and are weak in proportion to the amount of bitumen present.

TABLE II

Vulcanisation Tests on Rubber-Bitumen Samples

Sample	Time of vulcanisation at 148°C. (min.)	Elongation (per cent.)		Tensile Strength (lb./sq.in.)
		at 0.6 kg./sq.mm.	at break	
B	120	752	872	1540
	140	703	792	1410
	160	—	515	510
D	120	852	980	1290
	140	790	863	1180
	160	771	775	830
E	120	940	945	890
	140	838	887	990
	160	816	859	990

Conclusion

It does not appear likely that mixtures of rubber and bitumen prepared on the plantations would have any commercial prospects.

Kuala Lumpur
13th April, 1934

OBJECTIONS TO THE USE OF PARANITROPHENOL IN THE PREPARATION OF CREPE RUBBER

The undesirable shade of colour imparted to crepe rubber by paranitrophenol has in itself effectively prevented the adoption of this substance in the preparation of crepe rubber by Malayan producers. In Ceylon, however, where at certain times of the year atmospheric conditions are less favourable to drying than in Malaya, a few estates have used a small amount of paranitrophenol as a mould preventive in the preparation of blanket crepe.

The India Rubber Manufacturers' Association has recently drawn the attention of the London Advisory Committee for Rubber Research (Ceylon and Malaya) to certain difficulties experienced by manufacturers who purchased crepe rubber in the preparation of which paranitrophenol had been employed.

It was indicated that when such rubber is employed in manufacture the finished product will always yield a coloured extract when treated with water and that, because of this fact, the paper wrappers in which certain articles are enclosed for distribution become seriously stained if storage and other conditions are moist. The purchaser of any manufactured article naturally looks with suspicion on a product which is enclosed in a stained and unattractive wrapper and, where the article is intended for a use which concerns food or hygiene, dissatisfaction cannot but be expected to arise. Further, the article itself may be considered dangerous by health authorities who enquire into the manufacture of pale rubber goods used for feeding bottles and similar articles.

In tests made by manufacturers and by the staff of the London Advisory Committee for Rubber Research (Ceylon and Malaya) on paranitrophenol-treated crepe rubber, supplied by the Director of the Rubber Research Scheme (Ceylon), it was found that these arguments against the use of paranitrophenol were well-founded.

Malayan producers should therefore note that there are other and more serious reasons for the non-employment of paranitrophenol besides that of the colour which it imparts to the raw crepe rubber, and they are advised to continue to avoid its use.

E. R.

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